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Cellulose diacetate-*graft*-poly(lactic acid)s: synthesis of wide-ranging compositions and their thermal and mechanical properties

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Abstract

Cellulose diacetate-*graft*-poly(lactic acid)s (CDA-*g*-PLAs) were synthesized successfully over a wide range of composition in combination of different ways of graft polymerization: a copolycondensation of lactic acid; a ring-opening copolymerization of L-lactide in dimethyl sulfoxide; and a copolymerization similar to the second, but in bulk, each initiated at residual hydroxyl positions on CDA. Differential scanning calorimetry revealed that all the copolymer products gave a single glass transition temperature T_g, which decreased sharply from 202 °C of the original CDA to ~60 °C, close to T_g of PLA homopolymer, with an increase in molar lactyl substitution (MS) to 8 corresponding to $w_{PLA} \approx 67$ wt% in PLA content. When the MS reached 14 ($w_{PLA} \approx 79$ wt%) or above, PLA side-chains of the graft copolymers became crystallizable at temperatures above their respective T_gs (48–58 °C) unlike the CDA-*g*-PLAs of MS ≤ 8. In tensile measurements conducted at 80–100 °C for film sheets of melt-quenched CDA-*g*-PLAs, it was observed that their drawability increased drastically with increasing PLA content and, at a certain w_{PLA} of MS ≥ 14, the elongation at rupture reached a maximum of ca. 2000%. The synergistic behaviour is discussed in correlation to the composition-dependent thermal characteristics of CDA-*g*-PLAs.

Keywords: Cellulose diacetate-*graft*-poly(lactic acid); Thermal behaviour; Mechanical property

1. Introduction

Cellulose acetate (CA) is one of important cellulose derivatives, widely spreading as an industrially established product. It has recently been reported that CAs with a degree of substitution (DS) of < 2.5 are conventionally biodegradable [1,2], so that new functionalization of CA may be expected not only in many chemical industries but also in agroindustrial, sanitary, and bio-related fields. However, this cellulosic material shows a high glass transition temperature, which results in limited thermal processibility. In practice, low molecular weight plasticizers are usually utilized for thermal molding of CA. A problem of this convenient method of plasticization may be bleading out of plasticizers, which manifests itself in the course of time. A method to overcome the drawback is blending CA compatibly with flexible polymers [3,4]. An alternative way may be the synthesis of thermoplastic derivatives of CA by graft reaction with a suitable substituent [5,6].

Graft copolymerization has been a practical way to modify cellulosic molecules and that to alter the surface character of woody materials. It may be appreciated as a useful method not only to improve some original properties of polysaccharides but also allow the product copolymers to show a novel functionality. In contrast to the case for unmodified cellulose, the relatively good solubility of CA in some organic solvents, but variable according to the DS, makes it possible to undertake the reaction in an appropriate, homogeneous system.

As for the monomer ingredient for grafting CA, the use of aliphatic hydroxy acids or lactones would be a promising approach from a viewpoint of conformity with environment. Poly(hydroxy acid)s with high molecular weights are well known as biodegradable polymers and have been synthesized by polycondensation of hydroxy acids [7], while 'living-like' polymerization of cyclic esters can be initiated in the presence of tin (II) 2-ethylhexanoate (Sn(II)Eht) by hydroxo-initiators [8], which should involve CAs except cellulose triacetate substituted completely.

Several researchers have reported on preparation of CA-*graft*-aliphatic polyesters [5,9,10]. In contrast to extensive

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structural and physical studies for block copolymers and polymer blends, however, systematic works dealing with morphology, thermal transition behaviour, mechanical property, and the like for such graft copolymers have been restricted to only a small number of systems including synthetic/synthetic polymer pairs [11]. In order to accomplish a fruitful functionalization of cellulosic graft copolymers, further efforts should be made to elucidate in detail the relationship between the copolymer compositions and properties.

In the present study, cellulose diacetate (CDA) was adopted as a CA backbone, and the aliphatic polyester graft was poly(lactic acid) (PLA) which is known to be highly susceptible to hydrolysis in alkaline solutions or with Proteinase K in Tris-HCl buffer [12]. To prepare graft copolymer samples, CDA-*g*-PLAs, with a wide range of modification, the following three methods of grafting were employed complementarily; i.e. (1) copolycondensation of lactic acid, (2) ring-opening copolymerization of L-lactide in dimethyl sulfoxide (DMSO), and (3) ring-opening copolymerization similar to the method (2), but in bulk without DMSO. A scheme of the thermal and tensile behaviours of CDA-*g*-PLA is completed as a function of copolymer composition over the entire range. Concerning the biodegradation behaviour of the graft copolymer, it will be described in a subsequent paper [13] in connection with the phase structure explored based on the present experimental data.

2. Experimental

2.1. Original materials

CDA (number-average molecular weight, $M_n = 35,000$) was kindly supplied by Daicel Chemical Industries Ltd. The average degree of acetyl substitution (DS) of the CDA was determined as 2.15 by ^{1}H NMR. Lactic acid (88.5% aqueous solution) was purchased from Nacalai Tesque Co. Ltd. L-lactide was provided from Shimadzu Co. Ltd. and purified by recrystallization from ethanol solution. Diphenyl ether, tin(II) 2-ethylhexanoate (Sn(II)Eht), dimethyl sulfoxide (DMSO), and other organic solvents were purchased from Wako Pure Chemical Industries, Ltd.; these were all guaranteed reagent-grade and used without further purification. A PLA homopolymer (LACTY, $M_n = 75,000$) was kindly supplied by Shimadzu Co. Ltd. and used as received.

2.2. Graft copolycondensation of lactic acid onto CDA

An aqueous lactic acid solution of 112.99 g amount (net content of lactic acid, 100 g ($\approx$ 1.11 mol)) was dehydrated at 150 °C in a flask under a pressure of 50–55 mmHg for 3 h. Subsequently, 10 g CDA equivalent to 38.4 mmol in anhydroglucose residue, 200 ml diphenyl ether as reaction solvent, and 0.1 g Sn(II)Eht as catalyst were added into the above dried monomer of lactic acid, whereupon, the flask was equipped with a Soxlet extractor filled with molecular sieves 3A. The solvent was vaporized and re-supplied through the molecular sieves to the reactor under reduced pressure. The system was heated in an oil bath thermoregulated at 150 °C with stirring, and azeotropic dehydration was carried out under a pressure of 10–15 mmHg for 1–36 h. After the grafting reaction continued over a prescribed time-period, 200 ml acetone was poured into the reaction mixture. The resulting homogeneous solution was added dropwise into a vigorously stirred, large excess of methanol or methanol/toluene mixture (7:3 in volume). Each graft product obtained as the precipitate was filtered, washed with methanol or methanol/toluene several times, and dried at 60 °C in vacuo for 48 h.

2.3. Ring-opening graft copolymerization of L-lactide onto CDA in DMSO solution

CDA (5.00 g; 19.8 mmol in anhydroglucose residue), L-lactide (28.54 g; 396 mmol in lactyl unit), and DMSO (100 ml) as reaction solvent were added into a flask equipped with the same apparatus as that used in the graft copolycondensation. The system was heated in an oil bath at 130 °C with stirring, and dehydration was carried out under a pressure of 50–55 mmHg for 4 h. After that, Sn(II)Eht (0.286 g) was added into the flask and graft polymerization was conducted at the temperature and pressure specified above over a selected time-period of 4–24 h (first step). Purification and drying of the product were performed according to a sequence of procedure similar to that in the graft copolycondensation. A part of the CDA-*g*-PLA product obtained by a 24 h-reaction was supplied to the second step of graft polymerization, which was done in the same way as in the 1st step, but the reaction time ranged from 4 to 20 h.

2.4. Ring-opening graft copolymerization of L-lactide onto CDA in bulk

Ring-opening graft copolymerization was also carried out without solvent, i.e. in bulk. A typical procedure was as follows: CDA (2.50 g; 9.91 mmol in anhydroglucose residue) and L-lactide (14.27 g; 198 mmol in lactyl unit) were added into a flask and dried at 60 °C in vacuo for 12 h. Subsequently, the flask was heated in an oil bath at 150 °C with stirring under a dried nitrogen atmosphere. After 1 h, the system became a transparent liquid and then Sn(II)Eht (0.143 g) was added thereinto. Continuous stirring was conducted for another 1 h, which is defined as a reaction time of the grafting. The resultant polymeric product was dissolved in chloroform (50 ml) and purified with methanol or methanol/toluene in a similar manner as above. The composition of CDA-*g*-PLA was controlled by varying the in-feed ratio of L-lactide/CDA.

2.5. Measurements

Molecular weight of each product of CDA-*g*-PLA was determined on a TOSOH HLC-8020 gel permeation chromatograph (GPC) equipped with a refractive index detector and two TSK-GEL GMHHR columns connected with each other. The measurement was conducted by using tetrahydrofuran (THF) as mobile phase at a flow rate of 1.0 ml min^{-1}. The concentration of test samples was 0.5% in THF and the quantity of injection was 0.8 ml. The system was calibrated with monodisperse polystyrene standards.

500 MHz ^{1}H NMR spectra of CDA-*g*-PLA samples were measured by using a Bruker ARX 500 NMR apparatus. The measuring condition was as follows: solvent, $CDCl_3$ or CF_3COOD; solute concentration, 30 mg ml^{-1}; internal standard, tetramethylsilane (TMS); temperature, 300 K; pulse width, 3.0 μs; number of scans, 32. The ^{1}H NMR data was used for determining the molar substitution (MS) and the degree of lactyl substitution (lactyl DS), defined as an average number of introduced lactyl units and that of hydroxyls substituted for lactyls, respectively, per anhydroglucose residue of CDA. Fig. 1 exemplifies a ^{1}H NMR spectrum obtained for a CDA-*g*-PLA sample. In the spectrum, we designate a resonance peak area derived from the methyl protons of acetyl groups as **A**, an area from internal methyl protons of lactyls in PLA side-chains as **B**, and an area from the terminal methyl protons of lactyls as **C**; then the values of MS and lactyl DS, and the average degree of polymerization of a lactyl side-chain (DPs) can be estimated by Eqs. (1)–(3), respectively.

$$\text{MS} = 2.15(\mathbf{B} + \mathbf{C})/\mathbf{A} \tag{1}$$

$$\text{lactyl DS} = 2.15\mathbf{C}/\mathbf{A} \tag{2}$$

$$\text{DPs} = \text{MS}/(\text{lactyl DS}) \tag{3}$$

where a numeral 2.15 denotes an acetyl DS of the original CDA used in this work. Accordingly, a PLA weight content (w_{PLA}) in the graft product can be calculated with a molecular weight (278.9) of CDA repeating unit and that (72) of lactyl unit, in the following way:

$$w_{\text{PLA}} = 72\text{MS}/(278.9 + 72\text{MS})100(\%) \tag{4}$$

Differential scanning calorimetry (DSC) was conducted with a TA Instrument DSC 2520 apparatus. The measurements were carried out by using 5–10 mg samples (previously dried at 60 °C) at a scanning rate of 20 °C min^{-1} under a nitrogen atmosphere, after calibration of the temperature readings with an indium standard. The samples were first cooled to −50 °C, heated to 250 °C (1st heating scan), and then immediately quenched to −50 °C. The second heating scans were run from −50 to 250 °C, to record stable thermograms.

Wide-angle X-ray diffraction (WAXD) measurements were carried out with a Rigaku diffractometer RINT2200V. A Nickel-filtered Cu Kα radiation was used at 40 kV and 30 mA. Diffraction intensity was measured in a range of $2\theta = 4–45°$.

Film sheets of CDA-*g*-PLA for tensile tests were prepared by using a Toyo-Seiki hot-pressing apparatus. For the molding at 180–220 °C, a pressure was applied to the respective molten sample gradually to reach 5.0 MPa in 3–5 min, and subsequently it was increased quickly to 15.0 MPa and this application was maintained for 30 s. Following that, as soon as the pressure was released, the sample was transferred to another compressing apparatus and quickly cold-pressed at 25 °C and 15.0 MPa for 2 min. After released again from the compressed state, the molded polymer sheet was finally conditioned at 20 °C and 60% RH for 48 h. Specimens of rectangular shape ($80 \times 5 \times 0.4$ mm^3) were cut off from the respective molded sheets in substantially amorphous state. Tensile behaviour was examined for those specimens at a selected temperature of 80–100 °C by using a Shimadzu Autograph AGS-5kNG equipped with a thermostatic chamber Shimadzu

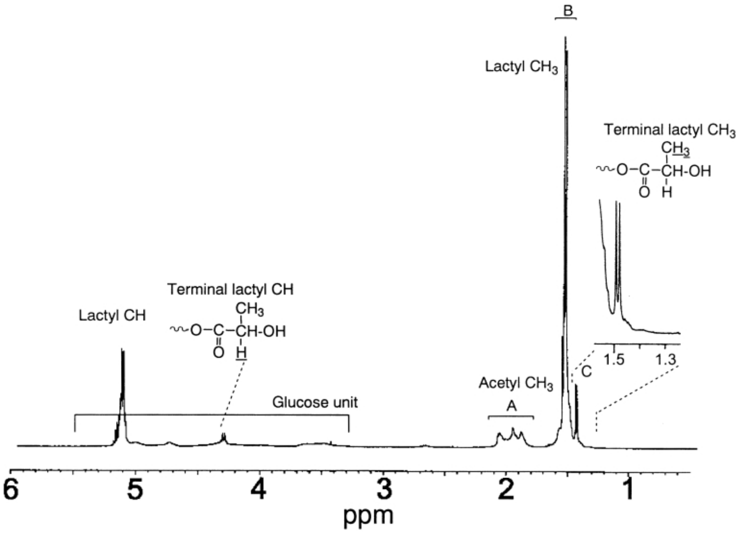

Fig. 1. ^{1}H NMR spectrum of a CDA-*g*-PLA with acetyl DS = 2.15, MS = 7.86, DPs = 8.93, and lactyl DS = 0.88.

TCH-220 + 250. The strain rate and span length were 0.5 mm min^{-1} and 40 mm, respectively. Five specimens of each CDA-*g*-PLA sample were employed for the measurement and the averaged data was adopted.

3. Results and discussion

3.1. Characterization of CDA-*g*-PLA products synthesized by three different copolymerization methods

3.1.1. Graft copolycondensation with lactic acid

Graft copolycondensation was conducted under reduced pressure of 10–15 mmHg in diphenyl ether as a reaction solvent. Water generated during condensation is efficiently removed by using the high boiling-point solvent under such a low pressure [7]. However, the system was essentially heterogeneous throughout the copolycondensation, due to deficient solubility of CDA in diphenyl ether that is a good solvent for PLA.

GPC chromatograms showed that the crude products thus obtained contained lactic acid homo-oligomers whose number-average molecular weight increased to 10,000 with an elapse of the reaction time. In the case where the oligomeric by-product was not completely dissolved in methanol, a mixture of methanol/toluene (7:3 in volume) was used to remove the by-product. The GPC chromatograms demonstrated, furthermore, that no degradation of the CDA backbone chain occurred and the molecular weight tended to gain a constant increment inherent in the progress of the graft reaction under the present condition adopted. This was also the case for the graft products synthesized by the other two methods described below.

An insight was provided into a kinetic aspect of the graft copolycondensation reaction. Fig. 2 shows a result of monitoring the variations of MS, lactyl DS, and DPs values for the products as a function of reaction time. It is found from the plots that a relatively longer side-chain (DPs ≈ 4) was already introduced onto CDA at an earlier stage of the reaction, in spite of the attainment of lower lactyl substitution. With a lapse of 3.3–12 h, the MS and lactyl DS increased progressively, whereas the DPs decreased. This indicates that the substitution of residual hydroxyls on the CDA backbone took place more efficiently during the time period than in the case of the earlier stage, possibly owing to enhancement of the affinity of CDA for the solvent diphenyl ether following the grafting of some amount of lactyl units. After 12 h, all the values of MS, lactyl DS, and DPs increased monotonically with reaction time and rose up to 3.15, 0.565, and 5.57, respectively, when 36 h passed. Thus an adequate selection of the grafting time in a range of ≤36 h led to the successful arrangement of CDA-*g*-PLA samples with different MS's of <3.2 converted as $w_{\text{PLA}} <$ 45 wt%. In the practical term of reaction time, however, a percentage of the actually grafted monomers was less than 11 mol%, because a large amount of lactic acid was consumed in homo-oligomerization initiated at the hydroxyl group of the monomer itself.

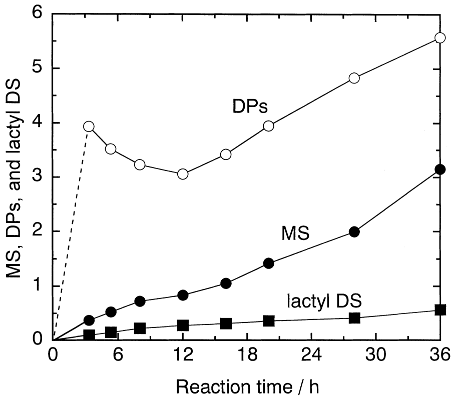

Fig. 2. Reaction-time dependence of MS, DPs, and lactyl DS for CDA-*g*-PLA samples synthesized by graft copolycondensation of lactic acid onto CDA. Grafting condition: in-feed weight ratio of lactic acid to CDA, 10; reaction temperature, 150 °C; catalyst content, 0.1 wt% relative to lactic acid; pressure, 10–15 mmHg.

3.1.2. Ring-opening copolymerization of L-lactide in solution with DMSO

A possible route to improve the grafting efficiency of lactyl moiety is the use of an alternative monomer L-lactide, which is known to exhibit a ring-opening polymerization with an initiator of hydroxyl compound in the presence of Sn(II)Eht as catalyst [8]. The ring-opening graft copolymerization of L-lactide onto the hydroxyl positions of CDA was conducted with DMSO as solvent, which served to lower the viscosity of the reaction system. GPC chromatograms confirmed that the employment of L-lactide provided no oligomeric by-product.

Fig. 3 shows plots of MS, lactyl DS, and DPs against time for this reaction system. A half of the data was obtained via two steps of the graft reaction, according to the procedure described already. In application of the 1st step only (reaction time ≤24 h), both MS and DPs values increased

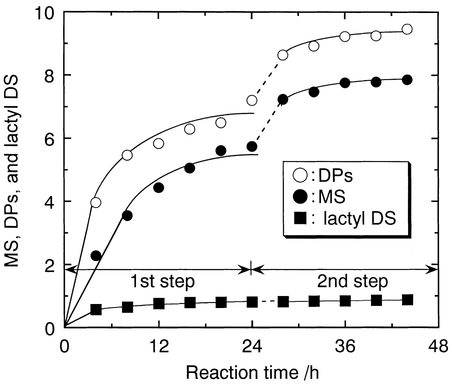

Fig. 3. Reaction-time dependence of MS, DPs, and lactyl DS for CDA-*g*-PLA samples synthesized by ring-opening graft copolymerization of L-lactide onto CDA in DMSO. Grafting condition: in-feed molar ratio of lactyl unit to anhydroglucose residue of CDA, 20; reaction temperature, 130 °C; catalyst content, 0.1 wt% relative to L-lactide; pressure, 55 mmHg.

rapidly until 12 h elapsed, then gradually increased with the passage of reaction time. When 24 h passed, the MS, DPs, and lactyl DS reached 5.75, 7.21, and 0.798, respectively. These values are all considerably large compared with the corresponding ones in the graft copolycondensation of lactic acid, suggesting that L-lactide has a higher reactivity than lactic acid.

The CDA-*g*-PLA obtained by the 24 h-reaction was supplied as a starting polymer material for the second-step graft reaction. In Fig. 3, the data are connected with the corresponding ones in the 1st step by broken lines. As can be seen from the plots, MS and DPs values initially rose abruptly, and their increments became slightly at an earlier stage of this second step. The observed tendency toward saturation is substantially similar to that in the 1st step. By adopting this two-step procedure of the graft copolymerization of L-lactide with DMSO, CDA-*g*-PLA samples of $\mathrm{MS} \leq 8$ and $w_{\mathrm{PLA}} \leq 67$ wt% were obtained in a practical time scale of reaction.

As has been experienced [5], ring-opening copolymerization of L-lactide can be completed very rapidly, e.g. in a few tens of minutes at ~ 140 °C, without any solvent under a strictly anhydrous condition. The present reaction in the coexistence of DMSO, however, yielded a continuous increase in MS of the product until at least 24 h passed. This observation indicates that DMSO is apt to suppress the reactivity of L-lactide for ring-opening graft copolymerization, to make the progress apparently moderate.

3.1.3. Ring-opening copolymerization of L-lactide in bulk

In order to obtain CDA-*g*-PLAs with longer side chains, a ring-opening copolymerization of L-lactide was conducted in bulk without DMSO at 150 °C over a period of 1 h. The system became gradually viscous and finally almost solidified. A changing manner of the compositional parameters of the graft products with variation of the in-feed molar ratio of L-lactide/CDA was examined for the 1 h-reaction. The result of the characterization is summarized in Table 1. It is found from the data that the bulk copolymerization gives rise to an increase in the MS value almost in proportion to the amount of L-lactide monomer in-fed. Accordingly, the PLA content in resulting CDA-*g*-PLAs appears to be controllable solely by changing the in-feed ratio of L-lactide/CDA adequately, and, in principle, an arbitrary extension of the side-chains would be possible in the ring-opening copolymerization in bulk. Actually, however, when the L-lactide/CDA ratio was lower than 10:1, the viscosity of the initial reactant mixture was too high to make the reaction homogeneous. To overcome this disadvantage, the addition of suitable solvent is required; a slower progression of the homogeneous graft-reaction is decidedly favorable for controlling the MS of CDA-*g*-PLA by adjusting the reaction time, as has been demonstrated above as the second method.

Thus, it is concluded that CDA-*g*-PLAs can be prepared successfully over a wide range of MS values to cover almost the whole of CDA/PLA weight ratios by use of a set of the above-mentioned three methods. The composition-controlled preparation of CDA-*g*-PLAs may also be useful for exploring a behaviour of biodegradation, programmed based on a difference in the degradation rates between the CDA backbone and PLA grafts [13].

3.2. Thermal transition behaviour of CDA-g-PLA

The CDA-*g*-PLA samples prepared by the above three methods were examined in thermal analysis by DSC, to clarify the composition dependence of the transition behaviour. Fig. 4 displays thermograms of selected samples of CDA-*g*-PLAs in the second heating scan, together with the corresponding ones for unmodified CDA and PLA homopolymer. All the data exhibit a clear base-line gap reflecting the glass transition temperature T_g of the respective samples. The absence of plural T_gs in the thermograms of CDA-*g*-PLAs provides evidence that no phase separation occurs in the amorphous matrices of the copolymers in a scale of T_g-detection, usually assumed to be less than a couple of tens of nanometers [14]. It should be noted here that the DSC curves of all the copolymer products indicated no additional transition signal in the second scan, differing from the case of plain PLA; the latter sample exhibited an exothermic peak ascribed to a crystallization on heating above T_g, followed by a fusion of the developed crystals giving an endothermic DSC signal, as illustrated in Fig. 4.

The dependence of T_g on the copolymer composition is

Table 1
Compositional parameters of CDA-*g*-PLAs synthesized by ring-opening graft copolymerization of L-lactide onto CDA in bulk

Sample code	In-feed molar ratio ([Lactyl]/[Anhydroglucose residue])	MS[a]	DPs[a]	Lactyl DS[a]	w_{PLA} (wt%)	M_n of PLA side-chain[b] (10^3)
1	15/1	14.0	17.7	0.79	78.8	1.28
2	30/1	22.4	20.6	~1.0[c]	85.7	1.48
3	60/1	57.9	80.5	0.72	93.7	5.80
4	80/1	77.4	125	0.62	95.4	9.00

Reacted at 150 °C for 1 h under dried N_2 atmosphere by using 0.1 wt% Sn(II)Eht relative to L-lactide.

[a] Determined by ^{1}H NMR.

[b] Calculated with values of DPs and molecular weight of lactyl unit.

[c] Estimated with uncertainty due to a very small NMR signal of **C** relative to that of **B** (see Fig. 1).

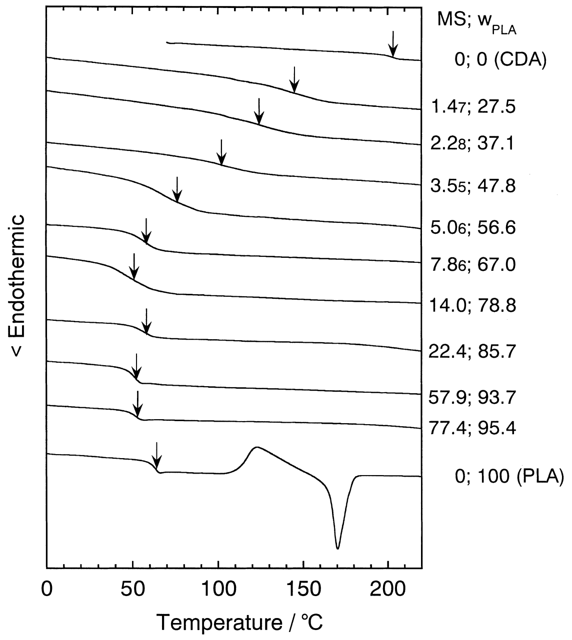

Fig. 4. DSC thermograms of CDA, PLA, and CDA-*g*-PLAs of various MS's, obtained in the second heating scan. Arrows indicate a T_g position taken as the midpoint of the discontinuity in heat flow.

made clear in Fig. 5 over the whole range of PLA content (w_{PLA}). The compiled data reveals a sharp depression of the T_g (202 °C) of CDA to the lower temperature side along with the increase in w_{PLA} to nearly 70 wt% (MS ≈ 10). The observation of a systematic variation of the single, composition-dependent T_g is quite similar to that for polymer blends in a good state of miscibility. However, the use of the term 'miscible' may be unsuitable for this series of CDA-*g*-PLAs, since a polymer pair of CDA and PLA never showed miscibility in the binary blends. In the present case, at least, it can be said that the PLA side-chains prevent assemblage of the CDA backbones and are able to play an effective role as 'internal' plasticizer to the originally semi-rigid cellulosic material.

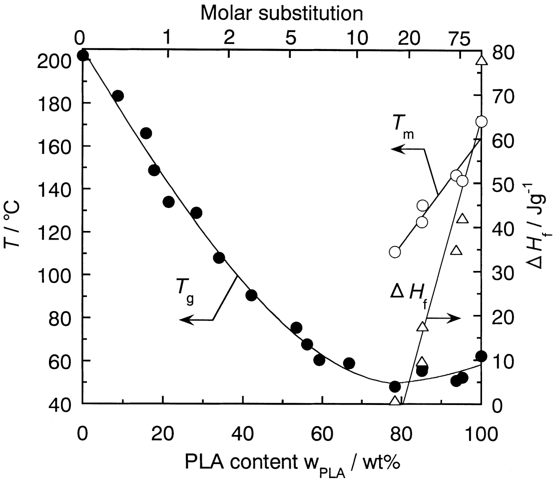

Fig. 5. Composition dependence of thermal transition parameters, T_g, T_m, and ΔH_f, estimated by DSC for CDA-*g*-PLA samples. Data of T_m and ΔH_f were obtained in the first run, while T_g was evaluated in the second.

As shown in Fig. 5, the copolymer T_g assumed a minimum of 48 °C at $w_{PLA} = 78.0$ wt% (MS = 13.7), and, with further increasing PLA content, it appeared to converge around a temperature somewhat lower than 62 °C that corresponds to the T_g of PLA homopolymer. At compositions of $w_{PLA} \geq 79$ wt% (MS ≥ 14), the DPs and therefore, the molecular weight of the attached PLA chains increased extraordinarily, as can be seen from the data listed in Table 1. It is therefore, reasonably inferable that two factors are in competition with each other regarding the T_g behaviour in the PLA-rich composition range: a lowering action of the copolymer T_g with increasing graft proportion; and a T_g elevation of the grafting PLA itself with abrupt prominence of the high-polymeric nature.

Another noteworthy behaviour was a crystallization habit observed for CDA-*g*-PLAs with longer PLA side-chains. Fig. 6 depicts DSC thermograms in the first heating scan for CDA-*g*-PLA samples with higher PLA contents (MS ≥ 14), compared in the same thermal history via a 60 °C-drying for 48 h. The respective thermograms of the PLA-rich copolymers show an endothermic peak centered at 110–150 °C, reflecting the melting of a crystalline phase, while the corresponding data for other samples with lower PLA contents (MS < 14) were essentially identical with the ones in the second heating scan. In the former samples of MS ≥ 14, it is very likely that an annealing-crystallization was induced during the drying process at 60 °C that is a little higher than their T_gs (48–58 °C). A value of DPs = 17.7, estimated for a crystallizable CDA-*g*-PLA sample of MS = 14.0, can be converted into a number-averaged molecular weight (M_n) of about 1300 (see Table 1), which is just comparable with an M_n permitting a linear polyethylene or nylon 6 to crystallize in a folded-chain fashion [15]. In a control experiment of annealing, it was ascertained that a sample of MS = 7.79, showing $T_g = 61$ °C, hardly crystallized even in heat-treatment at ~90 °C for more than 12 h.

Fig. 5 includes data of the composition dependence of the melting temperature T_m and of the enthalpy of fusion ΔH_f in

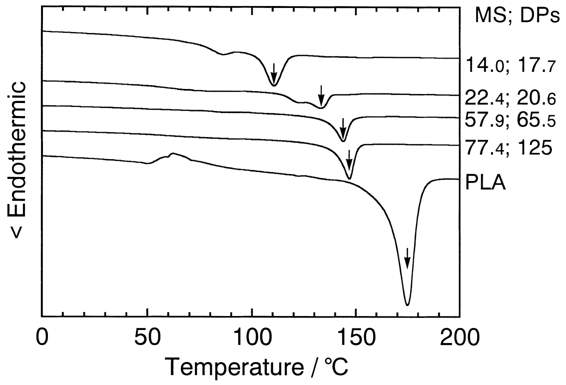

Fig. 6. DSC thermograms of CDA-*g*-PLA samples with different MS's. Arrows indicate a T_m position taken as the endothermic peak maximum.

the first heating scan, showing a monotonous increment of T_m and ΔH_f with an increase in PLA content above the critical crystallizable composition of $w_{PLA} \approx 79$ wt% and MS ≈ 14. The composition dependence of the crystallinity development in CDA-*g*-PLAs was also examined by WAXD measurements. Fig. 7 illustrates WAXD intensity profiles obtained for powder samples of original CDA, as-prepared CDA-*g*-PLAs, and PLA homopolymer, all heat-treated at 60 °C. The CDA-*g*-PLAs of MS < 14 solely impart a broad halo centering 18–20°, originated from an amorphous phase, and an additional feeble signal at $2\theta \fallingdotseq 8.5°$ derived from a nematic-like, ordered phase of the original CDA. In contrast to this, the PLA-rich graft copolymers of MS ≥ 14.0 provide a crystalline diffraction pattern, which is essentially similar to that for the PLA homopolymer and becomes sharper with lactyl content. Such an amorphous to crystalline transformation of the WAXD pattern with varying graft composition is in accordance with the DSC result in the first heating scan.

In addition to the composition-controlled preparation of CDA-*g*-PLAs described previously, their phase structure involving the crystalline development such as observed above will be a key factor affecting not only the biodegradability of the cellulosic copolymers but also the change in surface and internal morphology following the degradation [13].

3.3. Tensile properties of CDA-g-PLA

CDA-*g*-PLA sheets, which were obtained by melt-molding at 180–220 °C followed by quick cooling, were transparent to the naked eye irrespective, of composition. Strips cut from the film sheets were subjected to uniaxial stretching to find a relationship between the composition and the tensile properties. At room temperature, most samples were so brittle that their tensile behaviour could not be fully characterized. Therefore, the tensile data were collected at selected temperatures of 80–100 °C locating between the T_g of CDA and that of PLA homopolymer.

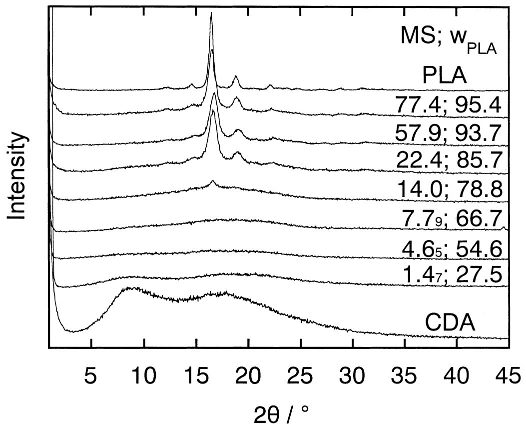

Fig. 7. WAXD profiles of CDA, PLA, and CDA-*g*-PLAs of various MS's, measured for their powder samples heat treated at 60 °C for 48 h.

Fig. 8 shows the composition dependence of three tensile parameters for sheets of the original CDA, CDA-*g*-PLAs, and plain PLA, measured at 90 °C. There appears a general tendency that tensile strength and Young's modulus decrease and elongation at rapture increases with increasing PLA content to ca. 80 wt%; however, their variations in the range of $w_{PLA} < 30$ wt% are of a small extent since the corresponding T_g values are considerably higher than the drawing temperature. At a composition of $w_{PLA} = 85$ wt% (MS $= 22$), the former two quantities assume their respective minima and the latter one a maximum, indicating that the ductility of CDA-*g*-PLA sheets becomes highest, as a maximal effect of plasticization caused by incorporation of PLA side-chains to the semi-rigid CDA backbone. It is surprising that the uniaxial deformation of the copolymer material reaches a draw ratio of as large as 20.

A further increase in PLA content beyond $w_{PLA} = 85$ wt% appears to rather depress the deformability of the CDA-*g*-PLA sheets. Obviously, the lowering of elongation at break is not the case experienced often in the drawing of extremely softened amorphous polymers [16], because the Young's modulus of the copolymer material becomes higher at a composition of $w_{PLA} = 95$ wt%, as is evident in Fig. 8. Thus a so-called strain-hardening takes place in the 90 °C-stretching of CDA-*g*-PLA sheets with the compositions of $w_{PLA} \geq 85$ wt% (MS ≥ 22). The PLA content of 85 wt% corresponds to that at which the annealing-crystallization of the graft side-chains becomes conspicuous at temperatures above the T_g of the CDA-*g*-PLA copolymer (see Figs. 5 and 7).

Results of the tensile tests conducted at 80 and 100 °C are given in Fig. 9; especially, the dependence of elongation at break (Fig. 9(a)) and that of Young's modulus (Fig. 9(b)) on the composition are compared with the corresponding data obtained at 90 °C in a PLA-rich range ($w_{PLA} \geq 60$ wt%). Of

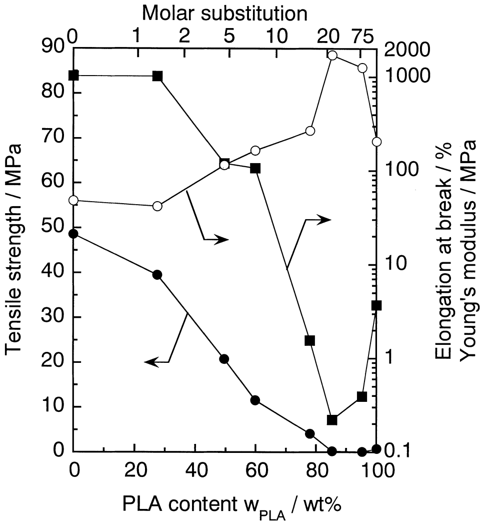

Fig. 8. Composition dependence of tensile strength, elongation at break, and Young's modulus measured at 90 °C for melt-molded sheets of CDA, CDA-*g*-PLAs, and PLA homopolymer. ●, Tensile strength; ○, elongation at break; ■, Young's modulus.

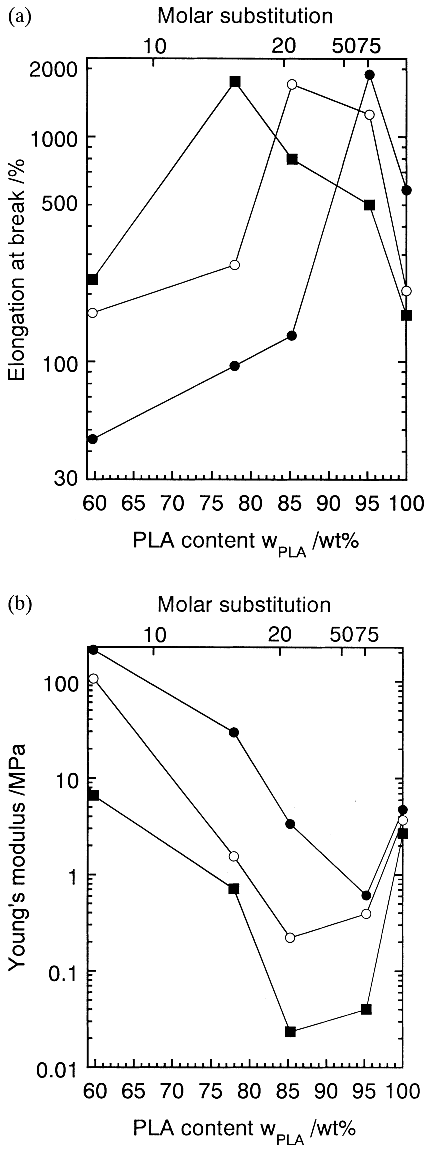

Fig. 9. Composition dependence of (a) elongation at break and of (b) Young's modulus for CDA-*g*-PLA sheets with PLA-rich compositions, showing a comparison between three sets of data obtained at different temperatures: ●, 80 °C; ○, 90 °C; ■, 100 °C.

particular interest is the finding of a shift of the maximum of elongation toward the lower w_{PLA} side with elevating temperature of drawing. Correspondingly, the location of a minimal modulus also tends to shift to lower PLA contents as the drawing temperature is raised, although the absolute modulus decreases in the order of increasing temperature at any composition.

In a detailed study on the isothermal crystallization kinetics for PLA-rich graft copolymers of $w_{\mathrm{PLA}} > 75$ wt% [13], we observed that the crystallization rate increased with an increase in PLA content, but much lower than that for plain PLA by two orders of magnitude, and that the fastest growth was attained at a temperature of 105–125 °C in a measurement range of 85–130 °C. The above result of the tensile testing would be correlated with the composition- and temperature-dependence of the crystallization kinetics. For example, the lowering of the drawability at a copolymer composition of $w_{\mathrm{PLA}} = 95$ wt% (MS = 77) with elevating temperature from 80 to 100 °C may be interpreted as due to a more rapid crystallization kinetics at 100 °C, and the devolution of the drawability at 100 °C with increasing w_{PLA}, observed above 78 wt% (MS = 13.7), may be consistent with the more prevalent crystallization at higher PLA contents.

It is thus plausible to assume that the change in ductility into suppression observed for PLA-rich compositions was given rise to by the crystallization of PLA side-chains induced during stretching at temperatures higher than the T_gs of the relevant graft copolymers. In DSC and WAXD measurements carried out after the tensile tests, however, even the drawn samples of $w_{\mathrm{PLA}} = 95$ wt% (MS = 77) exhibited no clear signal of crystalline phase evolution. Taking into account the less development of well-defined crystallinity, it can be suggested that rather fine, embryonic crystalline domains are dispersed to play a role of cross-linking points in the CDA-*g*-PLA sheets under deformation. The relatively small extent of dependence of the modulus and of elongation at break of the plain PLA sheet on drawing temperature provides an evidence of its more rapid crystallization; actually, the crystallinity was detectable explicitly for any of the stretched film specimens.

4. Conclusions

A connective use of the three methods to graft PLA on CDA, i.e. copolymerization of lactic acid, ring-opening copolymerization of L-lactide with DMSO, and similar copolymerization of L-lactide in bulk, met with success to synthesize CDA-*g*-PLAs over a wide range of MS's covering almost the whole of CDA/PLA weight ratios. The CDA-*g*-PLA products exhibited a composition-dependent, single T_g in the respective DSC thermograms. The T_g decreased from 202 °C of the original CDA to ~50 °C with increasing PLA content up to $w_{\mathrm{PLA}} \approx 79$ wt% (MS ≈ 14) and converged a little under the T_g (62 °C) of PLA homopolymer with a further increase of the lactyl content. Grafting a larger amount of lactyl units (MS ≥ 14) on CDA rendered PLA side-chains of the copolymers crystallizable, as the habit was ascertained by DSC and WAXD measurements.

The tensile tests conducted at 80–100 °C, intermediate between the T_gs of the two constituent polymers, revealed that the ductility of melt-molded CDA-*g*-PLA sheets increased with increasing PLA content and reached its maximum at a certain composition of $w_{\mathrm{PLA}} = 79$–95 wt%, which shifted to lower PLA contents with elevating temperature of the drawing. Above the critical PLA content, the film sheets became less drawable, possibly due to occurrence of some extent of crystallization of longer PLA side-chains of the copolymers under stretching.

The above results of the DSC and tensile measurements may be of great significance from the viewpoint of synergistic improvements in thermal and mechanical properties of both CA and PLA; the former shows a poor thermal processibility and the latter polyester has a nature of insufficient impact resistance coming from the less ductility. The present data also make a basis for further characterization of the cellulose derivative-aliphatic polyester graft as a promising biodegradable material. The degradation rate would be widely variable not only by altering the copolymer composition but also by controlling the phase structure involving crystalline morphology. Kinetic studies on the isothermal crystallization and enzymatic or alkaline hydrolysis of CDA-*g*-PLAs are topics that remain to be reported in no distant future [13].

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