ORIGINAL ARTICLE

Mariko Yoshioka · Katsuya Okajima · Tomoko Miyazaki
Nobuo Shiraishi

Plasticization of cellulose derivatives by reactive plasticizers II: characterization of plasticized cellulose acetates and their biodegradability

Abstract A plasticization method for cellulose acetates (CAs) has been developed that is based on the reaction with dibasic acid anhydrides and monoepoxides during the melting processing. As a continuation of the discussion in the previous report, additional evidence is presented for the role of grafting oligoesters onto cellulose acetates to prevent the bleeding of homo-oligoesters from the inside of molded articles to their surface. Based on these results, a method for enhancing the amount of grafting has been pursued by varying the combination of dibasic acid anhydrides and monoepoxides. The resulting reactive melt-processing method allows preparation of biodegradable cellulosic plastics using practical process conditions. Higher biodegradability has been found for the oligoester-grafted CAs than for the unmodified parent CAs.

Key words Plasticization · Cellulose acetate · Dibasic acid anhydride · Monoepoxide · Biodegradability

Introduction

Synthetic polymers are now used widely in our daily life, enriching living conditions. The use of these polymers, however, has caused environmental pollution problems. For this reason the development of biodegradable polymers is being actively pursued. These biodegradable polymers not only must be cost-effective, they must have performance characteristics comparable to those of

M. Yoshioka · N. Shiraishi
Graduate School of Agriculture, Kyoto University, Kyoto 606-8502, Japan

K. Okajima · T. Miyazaki
Toray Industries, Inc., Shiga 520-0842, Japan

N. Shiraishi (✉)
Graduate School of Agriculture, Kyoto University, Kitashirakawa Oiwake-cho, Sakyo-ku, Kyoto 606-8502, Japan
Tel. +81-75-753-6250; Fax +81-75-753-6300
e-mail: shiraish@kais.kyoto-u.ac.jp

common synthetic polymers and at the same time be degradable in the environment. These requirements are often mutually exclusive, and practical biodegradable polymers have not yet been realized.

With this background, we have developed a plasticization method for cellulose acetate (CA) that is based on the reaction with dibasic acid anhydrides and monoepoxides during melt-processing. In our previous paper[1] it was shown that CAs can be effectively plasticized by reactive melt-processing. To achieve effective plasticization, CA must be graft co-polymerized with oligomers (i.e., internal plasticization). Cellulose triacetate, which has no residual hydroxyl groups and no possibility to be grafted, could not be plasticized by this reactive melt-processing method.

It was also shown in the previous paper[1] that there is often a problem of (external) plasticizer bleeding. In this case, homo-oligomers prepared during melt-processing are not stable in the moldings, tending to migrate from the inside to the surface.

In this regard, it was suggested that grafting can effectively suppress or prevent the bleeding of nongrafted homo-oligoesters that are formed during grafting. It was reported in the previous paper[1] that cellulose monoacetate (CMA) more easily generates products with reduced bleeding than does cellulose diacetate (CDA), supposedly because the grafting proceeds to a higher level in the former case.

In this study the effect of oligomer grafting on reducing the bleeding of homo-oligomers was further explored by pursuing enhanced grafting efficiency. The biodegradability of the resulting oligoester-grafted CAs was examined.

Experiment

Materials

Cellulose acetates with different degrees of substitution (DSs), LL-10 and L-40, were supplied by Daicel Chemical

Industries Co. The DS of LL-10, monoacetate (CMA) (not utilized as thermoplastic), was 1.7–1.8; and that of L-40, diacetate (CDA) (commonly utilized as thermoplastic), was 2.4–2.5. Their degrees of polymerization were 100–200, and 160, respectively. Succinic anhydride (SA), maleic anhydride (MA), phenyl glycidyl ether (PGE), allyl glycidyl ether (AGE), and glycidyl methacrylate (GMA) were used as reactive plasticizing agents; sodium carbonate was used as the catalyst for the esterification when necessary; dimethylformamide (DMF) and methanol were used as the solvent and nonsolvent, respectively, for the purification of plasticized CAs. These reagents were extra pure or of guaranteed grade and were used as received.

Experimental methods

Reaction of CAs with plasticizers during melt-processing

Weighed amounts of CAs (LL-10 or L-40), dibasic acid anhydride (SA or MA), and monoepoxide (AGE, PGE, or GMA) were preliminarily mixed in a beaker. The mixture was then charged into a kneader (Labo Plastomill LPM 18–125; Toyo-Seiki Co.) that had been preheated to 80°–120°C while operating at 30 rpm for 5 min. The total amount of the mixture was 24 g, corresponding to the void volume of the mixing chamber of the kneader and causing torque while blending and reacting. After charging the mixture into the chamber, the rate of rotation was increased to 90 rpm, and the reaction in the kneader was performed within 10–40 min to obtain a plasticized sample.

Preparation of molded sheets

The kneaded samples were molded into sheets by hot pressing using a Toyo-Seiki 10t bench hot press. The samples (about 3 g) were placed between polyethylene terephthalate (PET) sheets with a 0.4 mm thick spacer. The temperature of the heated press was 180°–200°C. For molding, a gauge pressure of <5 MPa was applied slowly, taking 3–5 min before maximum pressure was reached to allow air bubbles to dissipate. The pressure was subsequently raised to 15 MPa and maintained for 30–45 s. The samples were cooled for 10–15 min to room temperature by cold pressing under the same pressure.

Tensile tests

Strips of samples, 80 × 5 × 0.4 mm, were cut from the molded sheets and were allowed to stand for more than 48 h at 20°C and 60% relative humidity (RH). The tensile tests were then performed using these conditioned samples and a Shimadzu Autograph DCS-R-500 under the same atmospheric conditions. The measurements were made using a span length of 40 mm and a cross-head speed of 0.5 mm/min. Average values were obtained from eight repeated measurements for the tensile strength, breaking elongation, and Young's modulus.

Purification of the plasticized CAs by the dissolution and reprecipitation technique

The melt-processed samples were dried and accurately weighed: A (g). These samples were dissolved in DMF (ca. 5 wt%) and reprecipitated in excess amounts of methanol. Then the reprecipitated products were kept in methanol under stirring overnight. After that, they were collected by filtration, and the precipitates were washed with water and dried to constant weights: B (g). The percent weight gains of CA were calculated based on the following equation.

$$\text{Weight gain of CA (\%)} = \frac{B\ (\text{g}) - \begin{array}{c}\text{calculated weight}\\ \text{of CA in } A\ (\text{g})\end{array}}{\begin{array}{c}\text{calculated weight of}\\ \text{CA in } A\ (\text{g})\end{array}} \times 100$$

Gel permeation chromatography analysis

The molecular weight distribution of the samples prepared as described in the above section; their purification products as well as the corresponding methanol-solubles, were determined on a TOSOH HLC-8020 gel permeation chromatograph (GPC) equipped with a refractive index (RI) detector using two TSK-GEL GMH$_{HR}$ columns connected in series. Measurements were conducted using tetrahydrofuran (THF) as the mobile phase at a flow rate of 1.0 ml/min. The concentration of test samples was 0.5% in THF, and the injected amount was 100 μl. The system was calibrated by monodisperse polystyrene standards.

Infrared spectroscopic measurements

A Fourier-transform infrared (FT-IR) spectrophotometer (Shimadzu FTIR-4000) was used for IR spectroscopic measurements. The technique used KBr disks for the measurements.

Flow tests

The thermal softening and flow behavior of the plasticized samples was observed using a flow tester (Shimadzu CFT-500A). The diameter and the length of the die used were 1 and 2 mm, respectively. The measurements were made at a constant heating rate of 10°C/min under a constant load of 5 MPa.

Viscosity measurements

The flow tester described above was used for measuring the melt-viscosity of the plasticized samples. The measurements were made at 200°C under a constant compressive load of 1 MPa.

Biodegradability tests

Soil burial test. Plasticized CA samples were buried in a standard soil composed of eight parts (by weight) of culture soil, one part of humus soil, and one part of vermiculite. The sample was buried in soil located in a room at constant temperature (30°C) and RH (80%); and the water content of the soil was adjusted to the original value (about 45%) by repeated watering. Strips of samples, 80 × 5 × 0.4 mm, were cut from the molded sheets and used for this testing. The soil burial test periods were 1, 3, 6, and 12 months. After each soil burial test the samples were washed and dried to their constant weights in a vacuum oven at 60°C. Then they were conditioned under the same conditions as those for test pieces for the above-mentioned tensile test and evaluated with regard to their external appearance, weight loss, and mechanical properties. High-density polyethylene (HDPE), cellulose triacetate (CTA), Japanese cedar, and polycaprolactone (PCL) were used as control samples in strip shapes.

Determination of oxygen consumption in a closed activated sludge suspension. Pulverized, plasticized CA samples were suspended within activated sludge, and oxygen consumption was measured by use of a coulometer, installed at Daicel Chemical Industries. An activated sludge obtained from the Himeji municipal sewage treatment plant was used.

Results and discussion

Role of grafting in preventing bleeding of the external plasticizer

In our previous paper[1] it was suggested that the larger the amount of grafting onto CA, the lower is the extent of bleeding of monomers and homo-oligomers toward the surface of plasticized CA moldings. The experimental evidence presented previously[1] was considered to be insufficient for unequivocal proof. Additional evidence must be uncovered.

Grafting and its role on bleeding

To confirm the occurrence of oligoester grafting, crude products obtained by the reactive melt-processing of CAs with dibasic acid anhydride and monoepoxides were first purified by the procedure described in the experimental section. That is, DMF solutions of the crude products were poured into excess amounts of methanol. Both the filtrate and the precipitate were analyzed after complete evaporation of methanol or after washing followed by drying, respectively. An example of the results is shown in Fig. 1.

In this case, 100 parts (by weight) of CDA, L-40, was reacted with 17.3 parts (by weight) of SA and 25.9 parts (by weight) of PGE at 120°C for 25 min under kneading conditions described in the experimental section. In Fig. 1 the reprecipitated material is found to cover only the high-
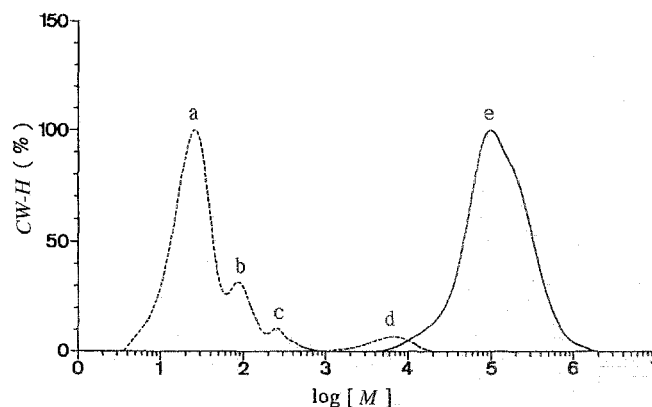

Fig. 1. Gel permeation chromatography (GPC) of reprecipitated SP-40 [cellulose acetate (L-40), succinic anhydride (SA), phenyl glycidyl ether (PGE)] and MeOH-soluble material of SP-40. SP-40: L-40/SA/PGE (100/17.3/25.9). Kneading: 120°C, 90 rpm, 25 min. *Solid line,* reprecipitated SP-40; *broken line,* MeOH-soluble material; *CW-H,* differential weight fraction expressed in height
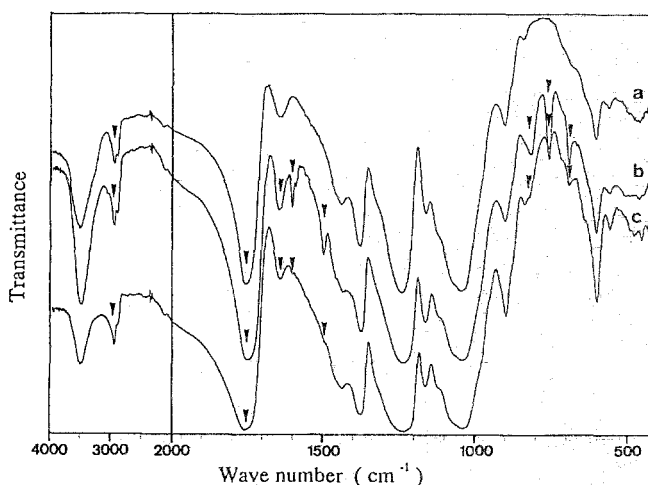

Fig. 2. Infrared (IR) spectra of reprecipitated MP-10 [cellulose acetate (LL-10), maleic anhydride (MA), PGE] and MP-40 (L-40, MA, PGE). MP-10: LL-10/MA/PGE (100/21.3/32.6); MP-40: L-40/MA/PGE (100/21.3/32.6). Kneading: 120°C, 90 rpm, 15 min. *a,* untreated LL-10; *b,* reprecipitated MP-10; *c,* reprecipitated MP-40. *Arrowheads* indicate related key bands

molecular-weight region (e). On the other hand, the methanol-soluble materials are found to cover the low-molecular-weight region (a–d). This provides clear evidence that the reprecipitated part contains only CA-related polymer and does not contain SA and PGE monomers or homo-oligomers. The filtrate can thus be said to be composed of monomers and homo-oligomers, with no high-molecular-weight matter (not including acetic acid).

Identical results were found in all other cases of these reactive melt-processing products, which implies that selection of the solvent and nonsolvent (i.e., DMF and methanol) was appropriate and that pure, grafted CAs can be obtained by this reprecipitation technique.

An attempt was made quantitatively to assay the extent of the grafting of oligoesters onto CAs. FT-IR spectroscopic measurements were used for these determinations. An example of the results is shown in Fig. 2. Here the IR

spectra of reprecipitated co-polymers obtained after melt-processing CMA or CDA with MA and PGE at 120°C for 15min are compared with that of CMA, one of the starting CAs. In this case, the spectra a, b, and c correspond to CMA (LL-10), oligoesterified CMA with MA and PGE (MP-10), and oligoesterified CDA with MA and PGE (MP-40), respectively. As is demonstrated by the results, a large number of absorption peaks not existing in the spectrum a are found in the spectra b and c. They include adsorption peaks at 700 and $750\,cm^{-1}$, being attributable to CH out-of-plane deformation vibrations of benzene rings with one substituent; peaks at 1500 and $1600\,cm^{-1}$ attributable to in-plane skeletal vibrations of benzene rings; peaks at $825\,cm^{-1}$ attributable to CH out-of-plane deformation vibrations of olefin having a side chain in its double bond portion; peaks at $1660\,cm^{-1}$ attributable to the stretching vibrations between C = C of the cis-form double bond; and so forth. These absorption peaks stem from MA and PGE and the corresponding grafting products.

In Fig. 2 it is also possible to compare the amounts grafted for LL-10 and L-40. The characteristic absorption peaks attributable to the grafted oligoesters appear more markedly for the oligoesterified LL-10 (curve b in Fig. 2) than for the oligoesterified L-40 (curve c). Thus, the supposition in the previous report[1] that more oligomer can be introduced into LL-10 than into L-40 finds further support, an observation that demonstrates that the co-polymerization capacity with homo-oligoester substituents is higher in the former case than in the latter.

Method for enhancing the grafting efficiency

After reaching the conclusion that it is the degree of grafting that controls the bleeding of homo-oligomers within the grafted CAs, it became of interest to study the possibility of whether the amount of grafting onto L-40 (CDA) could be increased by changing the conditions of reactive melt-processing.

First the reaction time was prolonged. Results obtained by FT-IR spectroscopy are shown in Fig. 3. The IR spectrum of purified MP-40 (L-40/MA/PGE = 100/16.9/25.9 by weight; 120°C) prepared by kneading for 20min (curve b) is compared with that prepared by kneading for 30min (curve c). The IR spectrum of untreated L-40 (curve a) is also shown. It is clear from the data that an increased amount of oligoester can be introduced into L-40 by increasing the kneading reaction time.

Because an increase in grafting amount with increased reaction time is demonstrated by IR spectroscopy, determining the actual grafting amount was pursued by measuring the weight increase of oligoesterified L-40 after purification.

The results are shown in Figs. 4–6 for MP-40, SP-40 (oligoesterified CDA with SA and PGE), and SG-40 (oligoesterified CDA with SA and GMA), respectively. Weight gains of L-40 after purification (amount of grafting) and the flow temperatures of the corresponding grafted products are shown as a function of the kneading time.
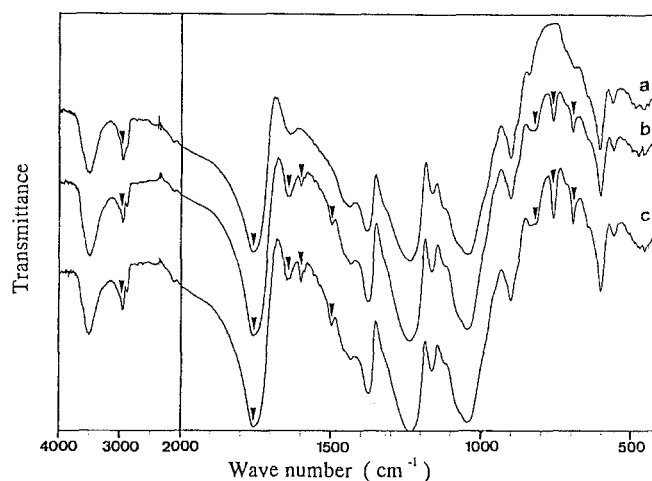

Fig. 3. IR spectra of untreated L-40 and MP-40. MP-40: L-40/MA/PGE (100/16.9/25.9). Kneading: 120°C, 90rpm, 20 or 30min. a, untreated L-40; b, reprecipitated MP-40 (kneading 20min); c, reprecipitated MP-40 (kneading 30min)
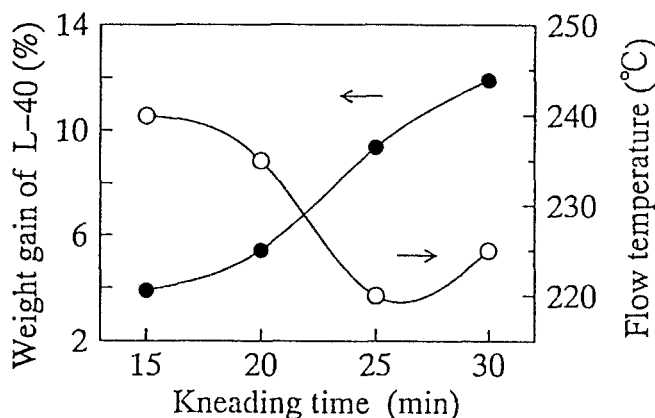

Fig. 4. Effect of kneading time with MA and PGE at 120°C on weight gain of L-40 and flow temperature of the grafted L-40. L-40/MA/PGE (100/16.9/25.9). Kneading: 120°C, 90rpm. Flow test: die diameter 1 mm, length 2mm; plunger 1cm²; load 5MPa; heating rate 10°C/min. *Filled circles*, weight gain of L-40; *open circles*, flow temperature
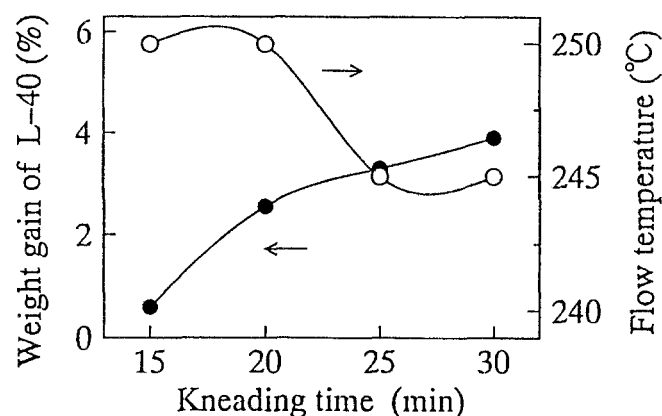

Fig. 5. Effect of kneading time with SA and PGE at 120°C on weight gain of L-40 and flow temperature of the grafted L-40. L-40/SA/PGE (100/17.3/25.9). Kneading: 120°C, 90rpm. Flow test: die diameter 1mm, length 2mm; plunger 1cm²; load 5MPa; heating rate 10°C/min. *Filled circles*, weight gain of L-40; *open circles*, flow temperature
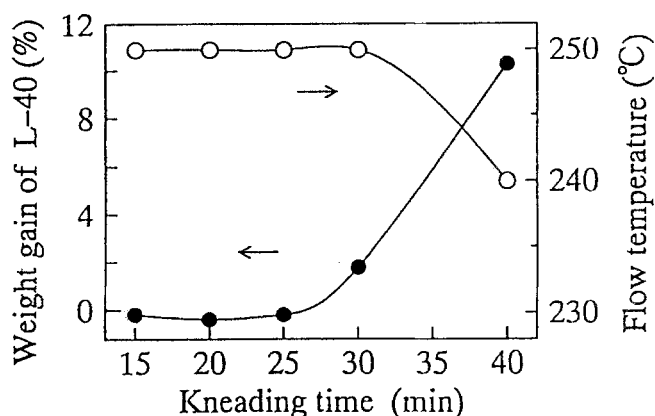
Fig. 6. Effect of kneading time with SA and GMA at 120°C on weight gain of L-40 and flow temperature of the grafted L-40. L-40/SA/GMA (100/17.7/25.1). Kneading: 120°C, 90 rpm. Flow test: die diameter 1 mm, length 2 mm; plunger 1 cm^2; load 5 MPa; heating rate 10°C/min. *Filled circles*, weight gain of L-40; *open circles*, flow temperature

Fig. 7. Effect of catalyst (Na_2CO_3) on weight gain of cellulose acetate. Kneading: 120°C, 90 rpm, 15 min. Flow test: die diameter 1 mm, length 2 mm; plunger 1 cm^2; load 5 MPa; heating rate 10°C/min. *A*: L-40/MA/ PGE (100/16.9/25.9) (30%). *B*: L-40/SA/PGE (100/17.3/25.9) (30%). *C*: L-40/SA/PGE (100/21.7/32.6) (35%). *D*: LL-10/SA/PGE (100/21.7/ 32.6) (35%). *E*: L-40/SA/GMA (100/17.7/25.1) (30%). Each percent value in parentheses shows reactive plasticizers content (wt%) in the starting material. *Open bars*, without catalyst (Na_2CO_3); *Shaded bars*, with catalyst (Na_2CO_3)

The weight gain and the flow temperature were found to depend on the reaction time in the kneader when all other conditions were kept constant. The data clearly illustrate that the amount of grafting increases with increasing kneading time for all reactive plasticizers used. The rate increase is especially significant in the case in which MA and PGE are used as plasticizers; there the weight gain was found to be almost linear, reaching 12% after 30 min of reaction. In contrast, when SA and PGE, or SA and GMA, were used for grafting, less weight gain was observed. A certain dependence on the species of reactive plasticizer is observed. However, even in the case of SA/GMA, in which the grafting amount up to 30 min was very low, the amount could be drastically increased when the reaction time was extended to 40 min.

These results can be attributed to the difference in the reactivities among the plasticizers. That is, MA is a more reactive dibasic acid anhydride than SA, and PGE is more reactive than GMA as a monoepoxide.

In accordance with the increase in the amount of grafting, the flow temperature decreases in every reaction system, confirming the effect of internal plasticization by grafting. The effect is especially significant when MA/PGE is used as the reactive plasticizer; the flow temperature was found to decrease by as much as 20°C after 25 min of kneading time. However, in the same reaction system, a small increase in the flow temperature is recorded between 25 and 30 min of reaction time, regardless of the steady increase in the amount of grafting. This might be explained in terms of a small degree of crosslinking or the formation or enhancement of side-chain interactions in the grafted CDA.

A second attempt to increase grafting efficiency focused on the addition of Na_2CO_3 as catalyst. The experiment attempted to accelerate the esterification between the hydroxyl groups of CDA and the acid anhydride. The results are shown in Figs. 7 and 8.

As is apparent, the observed increase in grafting (i.e., the weight gain of CA) and the reduction in thermal flow
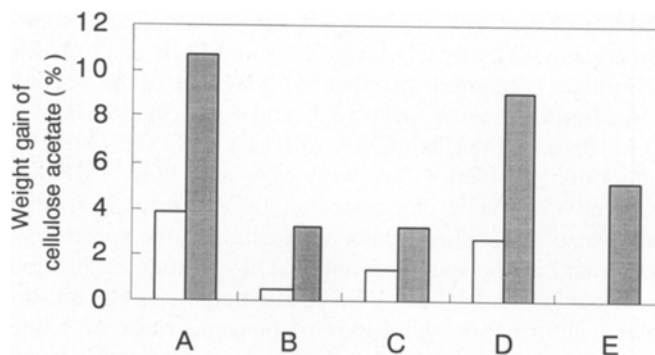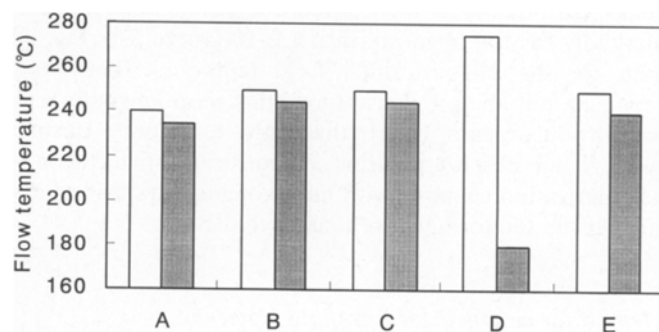

Fig. 8. Effect of catalyst (Na_2CO_3) on melt processability of the purified products. Kneading: 120°C, 90 rpm, 15 min. Flow test: die diameter 1 mm, length 2 mm; plunger 1 cm^2; load 5 MPa; heating rate 10°C/min. *A*: L-40/MA/PGE (100/16.9/25.9) (30%). *B*: L-40/SA/PGE (100/17.3/25.9) (30%). *C*: L-40/SA/PGE (100/21.7/32.6) (35%). *D*: LL-10/SA/PGE (100/21.7/32.6) (35%). *E*: L-40/SA/GMA (100/17.7/25.1) (30%). Each percent value in parentheses shows reactive plasticizers content (wt%) in the starting material. *Open bars*, without catalyst (Na_2CO_3); *Shaded bars*, with catalyst (Na_2CO_3)

temperature of the purified samples can be attributed to the addition of Na_2CO_3 in every plasticizer system used. However, the catalyst effect varies depending on the composition of the reaction mixture. That is, when the reactive MA/PGE system was used as plasticizer in combination with LL-10 (the sample that has a higher residual hydroxyl content than L-40,) the greatest grafting effect could be observed.

The catalytic effect of Na_2CO_3 on the physical properties of the melt-processed and molded products was also studied. The results are shown in Table 1. In each case the tensile strength and Young's modulus of the molded sheet increased, and the breaking elongation decreased with catalyst usage. At the same time both the melt viscosity and the apparent melt temperature of the melt-processed products increased. All these phenomena are interpreted in

Table 1. Effect of catalyst (Na_2CO_3) on physical and melt properties of the melt-processed products

Na_2CO_3 catalyst	Tensile strength (MPa)	Breaking elongation (%)	Young's modulus (MPa)	Melt viscosity (poise)	Flow temp. (°C)
L-40/MA/PGE (100/16.9/25.9)					
Without	37.2	23.9	1160	6110	165
With	49.9	10.8	1340	41570	185
L-40/SA/GMA (100/17.7/25.1)					
Without	34.4	30.8	1120	2400	145
With	50.8	11.5	1400	29820	165
L-40/SA/PGE (100/17.3/25.9)					
Without	29.9	25.5	1040	1580	165
With	31.3	15.9	1140	4500	170
L-40/SA/PGE (100/21.7/32.6)					
With	25.6	26.6	840	480	135
LL-10/SA/PGE (100/21.7/32.6)					
Without	39.3	29.6	1110	16500	140
With	43.1	23.5	1250	73090	165

Kneading: 120°C, 90 rpm, 15 min. Hot pressing: 190°C, 15 MPa, 5 min. Flow test: die diameter 1 mm, length 2 mm; plunger 1 cm^2; load 5 MPa; set tmperature 200°C; heating rate 10°C/min

L-40, LL-10, cellulose acetates; MA, maleic anhydride; PGE phenyl glycidyl ether; SA, succinic anhydride; GMA, glycidyl methacrylate

Table 2. Changes of sample properties during burial test in incubator

Parameter	Loss (%)			Tensile strength		Young's modulus		Elongation at break	
	Thickness	Width	Weight	MPa	Loss (%)	MPa	Loss (%)	%	Loss (%)
SP-10									
0 month	–	–	–	28	–	856	–	34.0	–
1 month	−29.6	−3.7	−40.6	6	79	72	92	47.7	−40.3
3 months	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
6 months	S.D.	S.D.	S.D.	S.D.	S.D.	S.D.	S.D.	S.D.	S.D.
SA-10									
0 month	–	–	–	31	–	996	–	22.6	–
1 month	−47.5	−2.7	−136.3	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
3 months	S.D.	S.D.	S.D.	S.D.	S.D.	S.D.	S.D.	S.D.	S.D.
MP-40									
0 month	–	–	–	45	–	1332	–	12.3	–
1 month	−2.6	3.7	8.7	46	−2	1879	−41	3.6	70.7
3 months	−0.8	6.2	12.8	57	27	1927	−45	4.2	65.9
6 months	−7.2	7.6	17.4	63	−40	2140	−61	4.2	65.9
12 months	−0.3	7.1	18.5	53	−18	2125	−60	4.0	67.5
MG-40									
0 month	–	–	–	36	–	1181	–	33.8	–
1 month	−10.9	6.9	10.9	27	25	972	18	22.6	33.1
3 months	−26.1	11.4	22.2	47	−31	1419	−20	5.4	84.0
6 months	−16.7	13.4	29.2	25	31	1458	−23	2.5	92.6
12 months	N.D.	N.D.	49.0	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
HDPE									
0 month	–	–	–	19	–	701	–	>50	–
1 month	−0.9	0.6	−0.1	20	−5	733	4	>50	0
3 months	0.6	0.9	0.0	19	0	618	13	>50	0
6 months	4.9	1.8	0.1	22	−16	695	12	>50	0
12 months	0.3	1.0	0.1	21	−11	753	−7	>50	0
PCL									
0 month	–	–	–	18	–	462	–	6.9	–
1 month	−2.8	1.2	1.4	17	6	555	−20	4.9	29.0
3 months	−7.3	2.3	3.2	15	17	579	−25	3.8	44.9
6 months	–	–	25.2	–	–	–	–	–	–
12 months	–	–	79.7	–	–	–	–	–	–
Japanese cedar									
1 month	−0.8	2.5	9.8	–	–	–	–	–	–
3 months	−0.6	1.7	8.9	–	–	–	–	–	–
6 months	−0.3	2.3	11.5	–	–	–	–	–	–
12 months	N.D.	N.D.	81.8	–	–	–	–	–	–

SP-10: LL-10/SA/PGE (100/21.5/32.3, w/w); kneading 120°C, 90 rpm, 20 min
SA-10: LL-10/SA/AGE (100/25.1/28.7); kneading 80°C, 90 rpm, 15 min
MP-40: L-40/MA/PGE (100/21.3/32.5), kneading 120°C, 90 rpm, 15 min
MG-40: L-40/MA/Gly (100/16.7/16.7), kneading 120°C, 90 rpm, 20 min
HDPE: "Mitsui Sekiyu Kagaku Co., "Hizex million 2100GP"
PCL: Daicel Chemical Industries, "PLACCEL H4"
N.D., could not be determined because samples were so deteriorated; S.D., samples disappeared

Fig. 9. Changes of high-density polyethylene (HDPE) and cellulose triacetate (CTA) specimens during the soil burial test in incubator
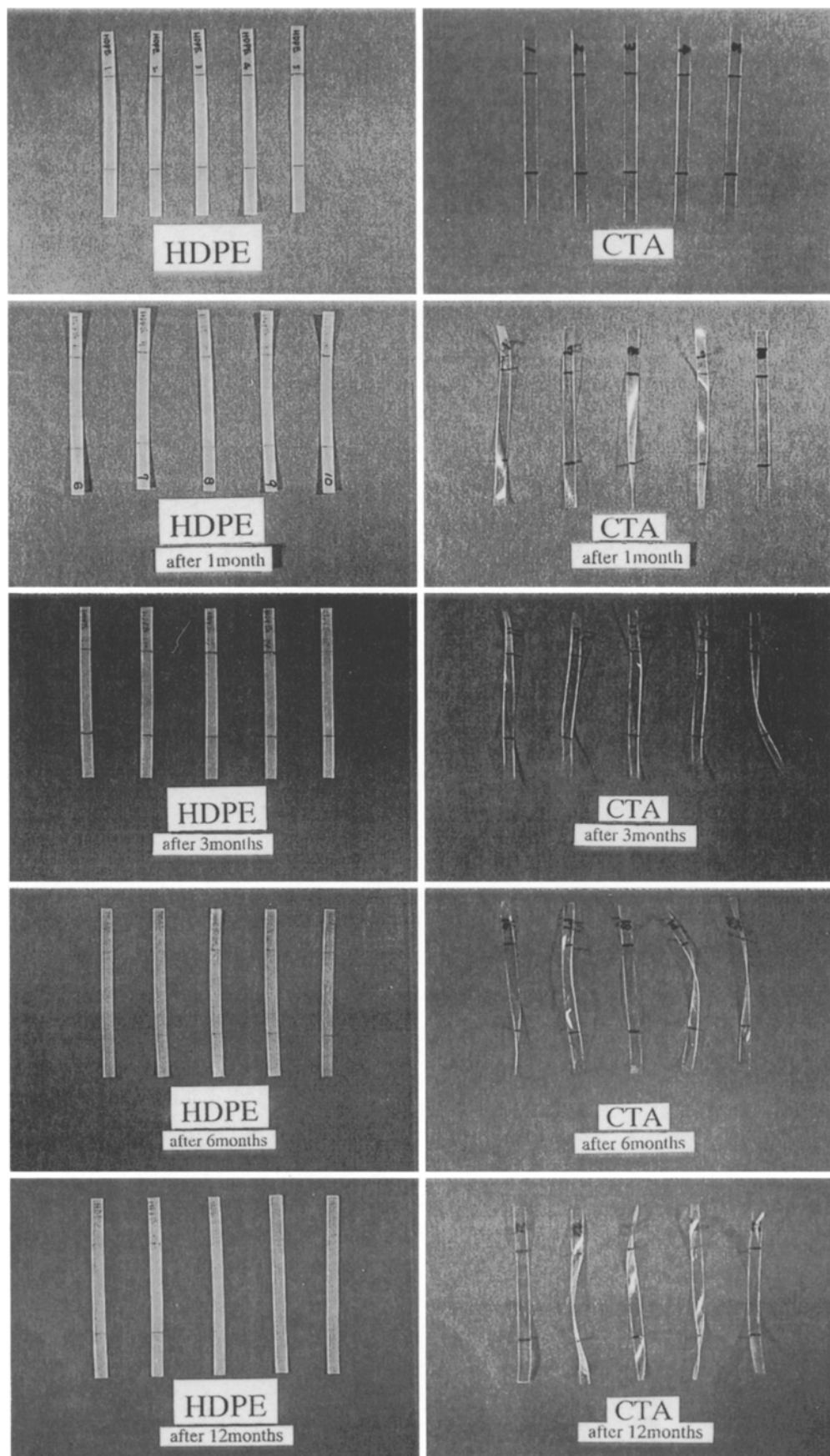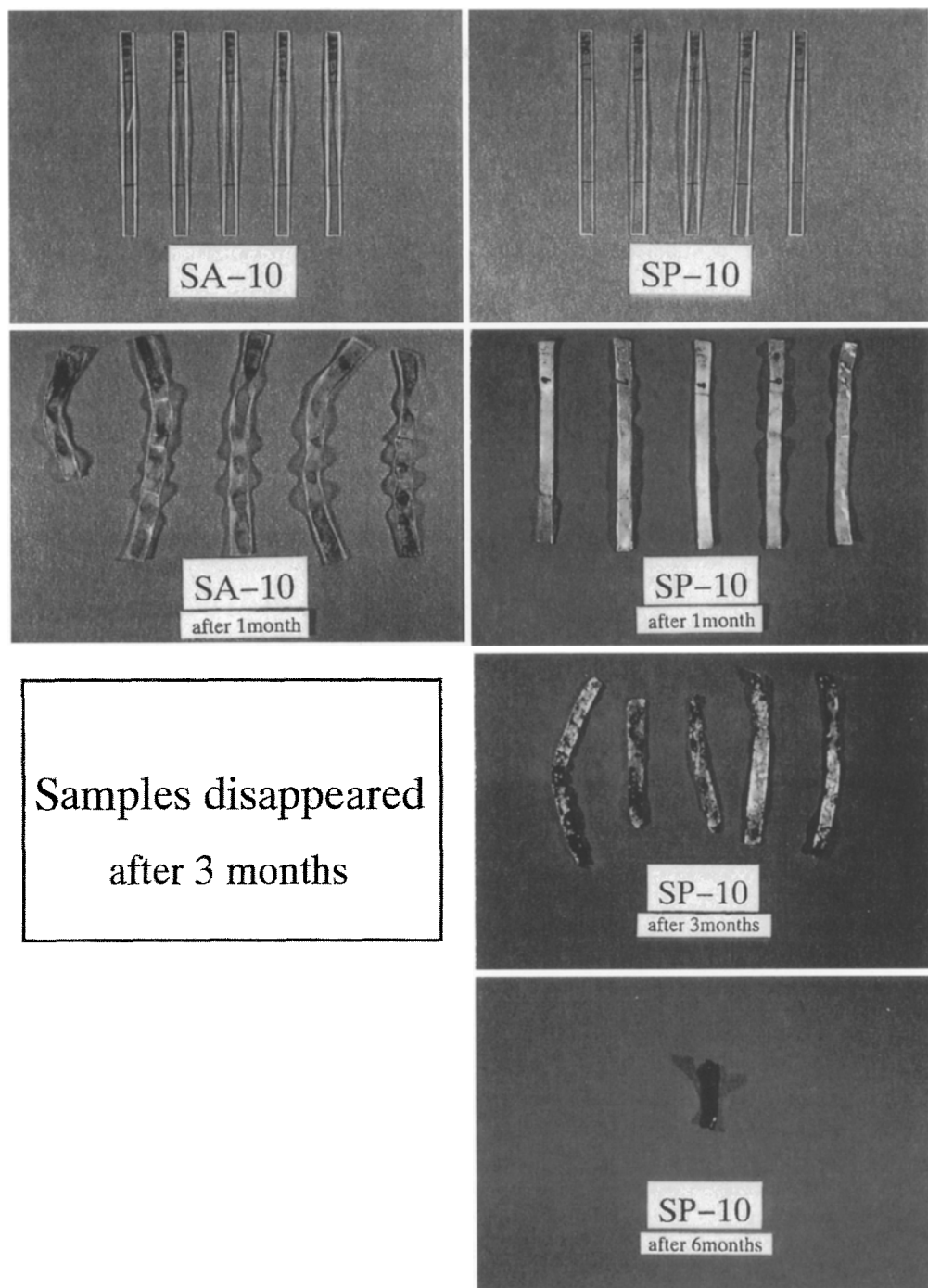
Fig. 10. Changes SA-10 and SP-10 specimens during the soil burial test in the incubator. The composition and preparation conditions of the samples are shown in Table 2

terms of the enhancement of grafting and the increased homo-oligomer molecular weights. Bleeding of monomers and homo-oligomers was no longer observed, and it was completely prevented in sheets prepared from the L-40/MA/PGE and the LL-10/SA/PGE melt-processed products shown in Fig. 7 and Table 1.

Biodegradability of CA plasticized by the oligoesterification

The plasticized CAs described above have been prepared by the use of reactive plasticizers considered biodegradable. Their preparation has also been based on the finding that CAs with a DS of up to 2.5 are biodegradable.[2-6] The biodegradability of modified CAs, however, should be demonstrated experimentally.

The results of various soil burial tests in terms of changes in external appearance and changes in physical properties are summarized in Table 2 and Figs. 9 and 10. The figures are examples of the results obtained.

Although the high-density polyethylene (HDPE) and cellulose triacetate (CTA) samples did not show biodegradability (Table 2, Fig. 9), plasticized CAs prepared in this study, as well as Japanese cedar and polycaprolactone (PCL), revealed distinct degradability (Table 2). In the case of plasticized CAs, the samples were degraded within relatively short times (i.e., 3–6 months). Plasticized CAs from CMA (LL-10) were damaged more easily than those from CDA (L-40). The former were completely degraded within 3–12 months; and before their disappearance the samples became cloudy and yellow, or their volume and weight increased. These changes can be explained by swelling, invasion of mycelia, and formation of internal voids. As degradation proceeds swelling progresses, and there is an increased mycelial invasion and accumulation, which prompts accelerated degradation. After 12 months, PCL was markedly degraded, leaving only several slivers; and plasticized CMA and CDA were either degraded completely or became cloudy. They yellowed, lost mass, and became brittle.

Overall, biodegradability was found to be affected by both the amount and type of reactive plasticizer used. As might have been expected from their chemical structures, the results indicated that among the dibasic acid anhydrides SA, lacking unsaturation and having no possibility of forming a crosslinking structure, was more degradable than MA; and that among the monoepoxides, AGE (being free of aromaticity) was easier to degrade than PGE. This means that by using glycerine in place of monoepoxide a more degradable oligoesterified CA can be achieved.

The biodegradability of powdered, oligoesterified CMA (LL-10) was also measured by determining oxygen consumption within a closed activated sludge suspension. The results are shown in Fig. 11. It is apparent that all samples are subject to significant biodegradation. The CMA control sample, LL-10, with a DS of 1.8 was degraded more slowly than any of the oligoesterified samples. The SA-10 sample,
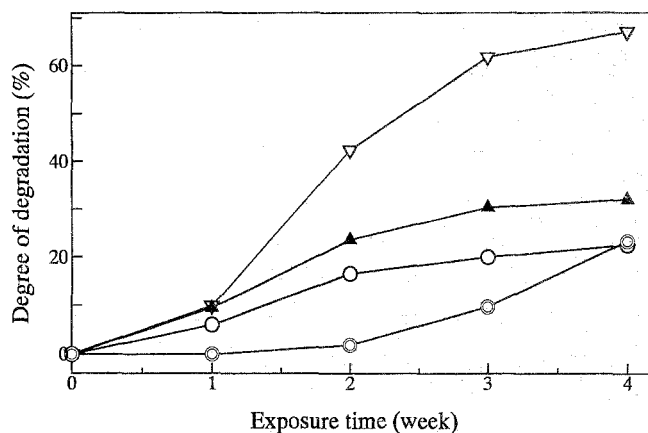

Fig. 11. Results of exposure to the closed activated sludge system. Degree of degradation was calculated using oxygen consumption and theoretical initial oxygen demand. *Double open circles,* LL-10; *single open circles,* SP-40: L-40/SA/PGE (100/11.0/25.9), kneading 120°C, 20 min. *Filled triangles,* MP-10: LL-10/MA/PGE (100/11.0/33.1), kneading 120°C, 20 min. *Open triangles,* SA-10: LL-10/SA/AGE (100/11.0/25.9), kneading 80°C, 15 min

which had shown the most pronounced degradation in the soil burial test (Fig. 10), also revealed the most rapid degradation by the oxygen-consumption test, reaching a value of 67% after about 4 weeks. This is higher than the value of 60% required for official acceptance of a novel chemical compound in Japan. Although this regulation is normally applied only to low-molecular-weight compounds – and in the case of polymers less stringent requirements are prescribed – the SA-10 sample was found to satisfy the requirement. The degree of degradation was found to decrease in the order of SA-10, MP-10, SP-40, and control (CMA). This is consistent with the results of the soil burial test mentioned above.

Conclusions

The following conclusions can be drawn from this study.

1. Using DMF as a solvent and methanol as a nonsolvent, crude grafting products could be purified.

2. Grafting of oligoesters onto CAs could be confirmed.

3. Direct evidence for the role of oligomer grafting onto CAs for preventing monomer and homo-oligomer bleeding has been obtained experimentally. That is, by increasing the amount of grafting, bleeding decreases.

4. Increases in the amount grafted could be achieved by extending the reaction period and by using an esterification catalyst.

5. Bleeding could be completely prevented in the CDA plasticized with MA and PGE as reactive plasticizers, and with Na_2CO_3 as esterification catalyst, that is, by employing reagents and conditions that maximize polymer modification by grafting.

References

1. Yoshioka M, Miyazaki T, Shiraishi N (1996) Plasticization of cellulose derivatives by reactive plasticizers. I. Mokuzai Gakkaishi 42:406–416
2. Buchanan CM, Gardner RM, Komarek RJ (1993) Aerobic biodegradation of cellulose acetate. J Appl Polym Sci 47:1709–1719
3. Komarek RJ, Gardner RM, Buchanan CM, Gedon SC (1993) Biodegradation of radiolabeled cellulose acetate and cellulose propionate. J Appl Polym Sci 50:1739–1746
4. Gu J, Eberiel DT, McCarthy SP, Gross RA (1993) Cellulose acetate biodegradability upon exposure to simulated aerobic composting and anaerobic bioreactor environments. J Environ Polym Degrad 1(2):143–153
5. Gu J, Eberiel DT, McCarthy SP, Gross RA (1993) Degradation and mineralization of cellulose acetate in simulated thermophilic compost environments. J Environ Polym Degrad 1(4):281–291
6. Gardner RM, Buchanan CM, Komarek RJ, Dorschel D, Boggs C, White AW (1994) Compostability of cellulose acetate films. J Appl Polym Sci 52:1477–1488