

Plasticization of Cellulose Diacetate by Reaction with Maleic Anhydride, Glycerol, and Citrate Esters During Melt Processing

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ABSTRACT: To accomplish the stable internal plasticization of cellulose diacetate (CDA), maleic anhydride (MAH) and glycerol (Gly) were used as reactive plasticizers. The plasticization method used was based on a melt-processing reaction of CDA with MAH and Gly. MAH and Gly (MG)-plasticized CDA showed stiff and brittle properties; that is, low elongation at break and high modulus. Thus, citrate esters were used as coplasticizers to improve physical properties. The resulted plasticized materials were optically clear, and showed attractive mechanical properties. The grafting of MG oligoesters to the free hydroxyl groups in CDA and their homo-oligomerization were accelerated by two-step kneading process, and verified by FTIR and GPC measurements. Differential scanning calorimeter (DSC) analysis revealed decreases of 80–100°C in the glass transition temperature (T_g) of CDA by these plasticizations. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 243–250, 2001

Key words: cellulose diacetate; plasticization; melt processing; citrate esters; oligoesters

INTRODUCTION

The development of biodegradable plastics has been accepted as one of the key solutions to reduce environmental problems caused by waste plastics. Natural polymers and their derivatives are recognized as a promising biodegradable material.^{1–4} Cellulose diacetate (CDA), the most commercially important cellulose derivative, was demonstrated recently as a biodegradable plastic.^{5–8} However, this material has a high glass transition temperature (T_g), which results in lim-

ited processibility compared to typical commodity plastics.

Thus, reducing T_g and the flow temperature of CDA are considered to be important. Traditional plasticization of CDA has been accomplished using conventional plasticizers such as phthalates, glycerol derivatives, phosphates, etc. These plasticizations often result in bleeding of the plasticizers, with their harmful character or problems of decomposition products. In this connection, there have been several attempts to utilize aliphatic polyesters as a plasticizer for cellulose acetates (CAs). In view of this situation, we have recently attempted to find novel plasticizers and plasticization procedures by which biodegradable thermoplastic polymers can be obtained from CAs.^{9,10} Attempts have been made to introduce

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oligoester chains into CAs during melt processing with dibasic acid anhydrides and monoepoxides. In these studies, it has been demonstrated that the oligoesterification of the free hydroxyl groups in the CAs results in internal plasticization. At the same time, external plasticization also takes place by homo-oligomerization between the dibasic acid anhydrides and the monoepoxides. However, bleeding of the external plasticizers was observed in these plasticized products, if the grafting by internal plasticization was not sufficient. In this case, the migrating plasticizers are chiefly homo-oligomers of acid anhydride and monoepoxide, and, also, a small part of remaining unreacted plasticizers.

It was the objective of this study to achieve more stable and safe plasticization of CDA by reactive plasticizers and to obtain the plasticized products having comparable mechanical properties to those of conventional plastics.

EXPERIMENTAL

Materials

CDA was supplied by Daicel Chemical Industries Co. Ltd., and its degree of substitution (DS) was 2.4–2.5. It was dried at 60°C under vacuum for 24 h. Commercial reagent grade maleic anhydride (MAH), glycerol (Gly), triethyl citrate (TEC), and acetyl triethyl citrate (ATEC) were used without further purification.

Plasticization of CDA

The plasticization reaction of CDA was principally performed by using Labo Plastomill LPM 18–125 kneader (Toyo-Seiki Co. Ltd.) under the following conditions: total amount of the mixture (CDA and plasticizers), 24 g; kneading temperature, 120°C; preheating time, 5 min; kneading time and rotation rate, 15–60 min and 90 rpm, respectively. Two modes of reactive processings were performed; that is, one- and two-step kneading processes. The detailed explanations of these two processes are shown later in this article.

Thermal Molding and Tensile Test

The kneaded products were hot pressed (190°C) by using a Toyo-Seiki bench hot press to obtain sheets for the tensile tests. For molding, pressure was slowly applied up to 5.0 MPa for 3 min, then was quickly raised to 15.0 MPa and maintained

for 30 s. Subsequently, the samples were cold pressed at 15.0 MPa, then were conditioned at 20°C and 60% RH for 48 h.

Specimens of rectangular shape (80 × 5 × 0.4 mm) were also obtained from the molded sheets. Tensile tests were performed on these specimens by using a Shimadzu Autograph AGS-5kNG at 20°C and 60% RH. The strain rate and span length were 0.5 mm/min and 40 mm, respectively. Ten specimens of each sample were measured, and the mean values were recorded.

Purification of Plasticized CDA

Purification of plasticized CDA was accomplished, when necessary, as follows. A vacuum-dried sample (5 g) was completely dissolved in 80 mL acetone with stirring for 24 h. The solution was slowly precipitated by pouring into 2 L methanol (MeOH), then filtering. The MeOH-soluble part (homo-oligomer and unreacted monomer) was analyzed by gel permeation chromatograph (GPC) and the MeOH-insoluble part (MG-grafted CDA) was analyzed by Fourier-transform infrared spectroscopy (FTIR).

GPC and FTIR Measurement

Molecular weight distribution curves were recorded by using an HLC-8020 GPC apparatus equipped with a differential refractometer detector. Eluent was tetrahydrofuran (THF) at 25°C using standard samples of polystyrenes. FTIR spectra were measured using a Shimadzu FTIR 4000 spectrometer. The KBr disk technique was employed to prepare the samples for the measurements. For each spectrum, 40 consecutive scans with a 2 cm⁻¹ resolution were performed.

Thermal Flow Properties

Apparent flow temperatures of the samples were measured by a constant rising temperature test with a flow tester Shimadzu CFT-500A under the following conditions: starting temperature, 50°C; rising temperature rate, 5°C/min; die orifice size; 1 mm diameter and 10 mm length. Apparent melt viscosity measurement were performed with the same equipment under a constant temperature (200°C).

Extraction of Plasticizers into Water

Three specimens per sample (50 × 50 × 0.4 mm) were cut off from the molded sheets and dried at

Table I Tensile Properties of MG-Plasticized Products Differing in the Amounts of Plasticizer

The Amount of Plasticizers (MG)	Tensile Strength (MPa)	Young's Modulus (MPa)	Elongation at Break (%)
20%	47.0	1337	7.5
25%	35.8	1037	19.3
30%	27.1	735	44.6

The molar ratio of MAH to Gly is 1 : 1.

50°C for 24 h. After cooling in a desiccator, the samples were accurately weighed and then sunk into 500 mL deionized water at $20 \pm 2^\circ\text{C}$ for 48 h. The samples were dried at 50°C for 24 h, and subsequently weighed after cooling in a desiccator. Extraction of plasticizers into water was determined by calculating its weight loss.

Differential Scanning Calorimeter (DSC) Measurement

The DSC thermograms were obtained using a TA Instrument DSC. The samples (around 10 mg) were placed in sealed aluminum cells. To provide the same thermal history, each sample was initially heated from room temperature to 250°C with a rate of 20°C/min under nitrogen atmosphere, then immediately cooled to -100°C with a 20°C/min rate. Second scan heating curves were then recorded by heating from -100 to 300°C with a 20°C/min rate. The T_g of each samples was evaluated from the second scan as the T_g midpoint, i.e., the T_g midpoint was adopted to be midpoint of the tangent between the intercepts formed by extrapolation of the baseline preceding and following the transition and the tangent of the transition.

RESULTS AND DISCUSSION

The authors studied the plasticization of CDA by reactive processing with MAH and monoepoxides in previous trials.⁹ By this modification, CDA could be converted to plastics with a range of properties. In this processing, homo-oligomers polycondensated from MAH and monoepoxides were free, and their bleeding caused by migration of these homo-oligomers often occurred. This problem was overcome by enhancing the grafting rates or amounts, as shown in the previous arti-

cle.¹⁰ This bleeding phenomenon is in general one of the most important and serious problems for realizing ideal plasticization of polymers by external plasticization. Therefore, it is important to continue the effort to find other methods for preventing the bleedings. In this study, we tried to use Gly instead of monoepoxides, and to examine whether it is effective for reducing the bleeding problem.

Furthermore, monoepoxides, especially when they are volatile, are considered to be dangerous as reagents because of their high reactivity toward proteins. This is another reason that we used Gly as an alternative reactive plasticizer for monoepoxides in the present melt processing of CDA. Gly is not reactive toward proteins in human eyes, for example.

A lot of experiments were carried out concerning the melt processing of CDA with MAH and Gly.¹¹ The products obtained by these experiments were known to have stiff and brittle properties, as indicated low elongation and high modulus (Table I). Thus, in the first part of this study, the authors investigated the thermoplasticization of CDA by melt processing with MAH, Gly, and citrate esters. In this case, TEC and ATEC were used as the citrate esters, separately, as the external plasticizers.

Effect of the External Plasticizer/Reactive Plasticizer Ratio

The total amount of plasticizer was fixed at 30% at the first stage of the experiment and the added ratio of citrate esters to MG was changed. The molar ratio of MAH to Gly was fixed at 1 : 1. In both the TEC/MG and the ATEC/MG series, transparent and clean sheets were obtained by hot pressing of the kneaded products regardless of the added ratio of plasticizer. A slight odor of acetic acid was smelled, and the bleeding of plas-

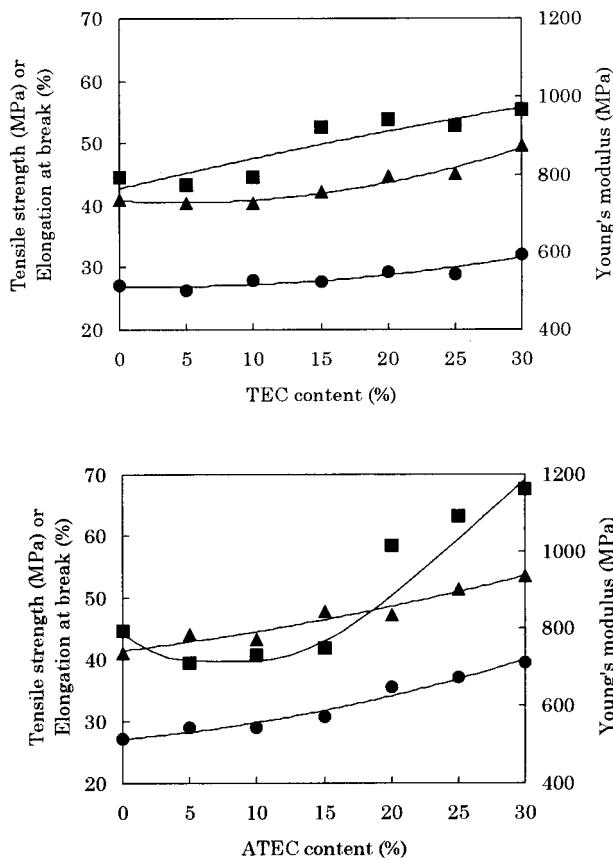


Figure 1 Effects of the added citrate esters ratio within plasticizers on tensile properties of the plasticized CDA. Total plasticizers amount is 30%, MAH : Gly = 1 : 1 (molar ratio). ● Tensile strength, ■ elongation at break, ▲ Young's modulus.

ticizers was occasionally observed. There is a possibility that the latter are caused by the presence of residual unreacted plasticizers. This point will be examined later by using reduced amounts of the plasticizers.

Tensile properties plotted as a function of the composition of plasticizers can be seen in Figure 1. It was found that all of the tensile properties are improved with an increase in the citrate esters content. CDA plasticized by MG has brittle properties when compared to that plasticized merely by citrate esters. Accordingly, it is considered advantageous to blend citrate esters to improve toughness of MG-plasticized CDA.

When the TEC/MG and ATEC/MG series are compared as shown in Figure 1, it was found that the ATEC/MG series was superior to the TEC/MG series in tensile properties. Furthermore, reaction temperature and torque for the ATEC/MG series were found to be higher than those of

TEC/MG series. These results can be explained in terms of the higher affinity of ATEC than that of TEC toward the MG-plasticized CDA.

In the second part of this experiment, the total amount of the plasticizers was reduced to 25%. The added ratios of the plasticizers and the molar ratio of MG were in the same ranges as described above. As was expected, the acetic acid odor was reduced and the unreacted monomers were diminished. Moreover, the temperatures during the reaction and torque yielded were higher than those of 30% total plasticizer. Consequently, oligoesterification was more effective. Figure 2 shows the mechanical properties of plasticized products obtained using 25% plasticizers. There was little dependence of the tensile strength and the modulus relative to the amounts of citrate esters added. However, the elongation at break was improved remarkably with increasing the ci-

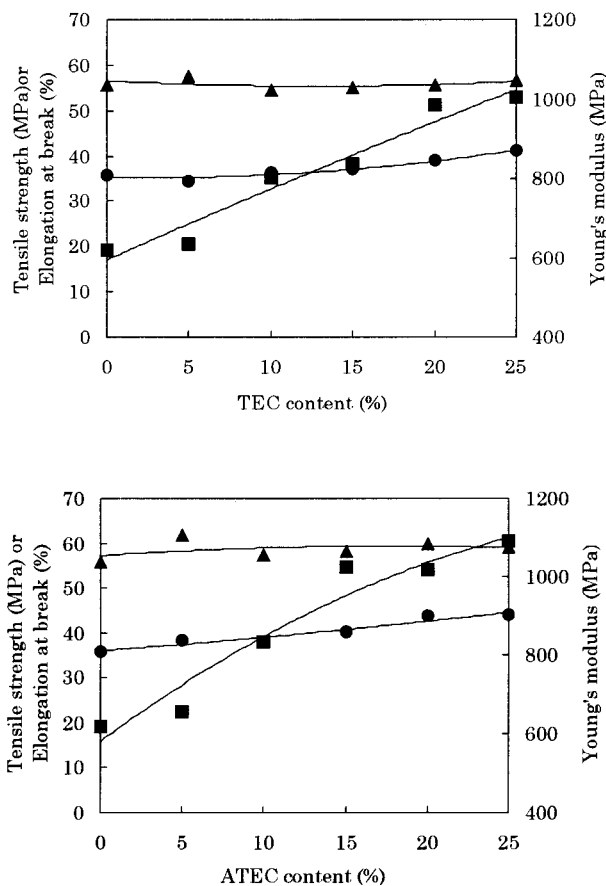


Figure 2 Effects of the added citrate esters ratio within plasticizers on tensile properties of the plasticized CDA. Total plasticizers amount is 25%, MAH : Gly = 1 : 1 (molar ratio). ● Tensile strength, ■ elongation at break, ▲ Young's modulus.

Table II Tensile Properties of Various Polymers Including Plasticized CDA and Synthetic Generally Used Polymers

Polymers	Tensile Strength (MPa)	Young's Modulus (MPa)	Elongation at Break (%)
MG/TEC, ATEC-Plasticized CDA	25–50	725–1334	20–67
LUNARE ^a	47	1510	38
Polystyrene	30	860	4
Polypropylene	30	740	>100
Polycaprolactone	21	160	400

^a Cellulose acetate plastic commercially sold by Mitsubishi Corporation.

trate esters content. As mentioned above, MG-plasticized products can be toughed by the simultaneous addition of the citrate esters.

At 20% total plasticizer addition, CDA was not completely plasticized due to an insufficiency of the plasticizers. Thus, the kneaded products were unsatisfactorily molded at the molding temperature of 190°C, which was lower than their flow temperatures (Table III). From these results, the 25% level of the plasticizers is considered as optimum.

The tensile properties obtained are comparable to or better than those of general synthetic polymers and commercially plasticized cellulose acetate, such as LUNARE, as shown in Table II.

The use of glycerol makes it possible to effect crosslinking reactions, because it has three reactive sites. This can be examined by the measurements of the thermal flow properties of the products. Thermal flow properties of CDA plasticized with 30, 25, and 20% levels plasticizers are tabu-

lated in Table III. Data in Table III suggest the possibility of the occurrence of a crosslinking reaction are very low because thermal flow properties do not show any evidence of the crosslinking reaction. It is also found that addition of the citrate esters can reduce melt viscosities and flow temperatures of the MG-plasticized CDA.

Comparison of One and Two-Step Kneading Processes

To accomplish more effective internal plasticization by grafting MG to free hydroxyl groups of CDA and to obtain the high molecular weight MG homo-oligoesters, a two-step kneading process was attempted. That is, in the first step, the reactive kneading of CDA and the reactive agents (MAH, Gly) was performed for 10 min, followed by the addition of external plasticizers (citrate esters) with further melt processing for 10 min. It was expected that the oligoesterification of MG

Table III Flow Properties of CDA Plasticized by MAH, Gly, and Citrate Esters

Total Amount of Plasticizers (%)	Composition (w/w)	Melt Viscosity (Poise)	Flow Temperature (°C)
30	MG/TEC 30/0	3039	164.2
	20/10	2252	158.7
	MG/ATEC 20/10	2864	166.2
25	MG/TEC 25/0	12,260	180.7
	15/10	4071	172.4
	MG/ATEC 15/10	4204	177.0
20	MG/TEC 20/0	19,510	198.2
	10/10	9795	190.3
	MG/ATEC 10/10	16,920	195.7
Control CDA	—	—	249.8

MG: MAH and Gly (1 : 1 mol), TEC: triethyl citrate, ATEC: acetyl triethyl citrate.

Table IV Tensile Properties of CDA Plasticized by One and Two-Step Kneading Processes

Adding Methods of Plasticizers	Composition (%)	Kneading Time (min)	Tensile Strength (MPa)	Young's Modulus (MPa)	Elongation at Break (%)
One-step kneading process	15MG/10TEC	20	35.7	845	43.9
	15MG/10ATEC	20	41.7	1023	40.7
Prolonged one-step kneading process	15MG/10TEC	60	39.3	1045	31.2
	15MG/10ATEC	60	46.6	1216	37.6
Two-step kneading process	15MG/10TEC	10 + 10	40.4	1057	31.9
	15MG/10ATEC	10 + 10	50.6	1335	19.9

can be advanced more effectively in the absence of inert additives (citrate esters).

As shown in Table IV, the plasticized CDA obtained by a two-step kneading process had higher strength and modulus than those attained by a one-step kneading process in the same reaction time. Elongations at break decreased in the two-step kneading. However, when kneading time was prolonged in the one-step kneading process, tensile properties were similar to those of the two-step kneading process. These results reveal that with an increase in MG grafting, a decrease in unreacted reactive monomers (MAH and Gly) and an increase in the molecular weight of homo-oligomers occurred. These gave enhanced stiffness in the products, when the two-step kneading process or the prolonged kneading time was adopted. It is quite evident that the oligoesterification of MG requires long kneading reaction time than in the one-step kneading process, but it is accelerated by using a two-step kneading process.

To verify the differences in the grafting reaction of these melt-processing methods, FTIR spectra of the plasticized CDA after removal of unreacted monomers, homo-oligomers, and citrate esters were obtained. As shown in Figure 3, for the samples obtained through the two-step process and the prolonged one-step process, relatively strong peaks of out-of-plane C—H bending belonging to the maleic anhydride appeared at 780 cm^{-1} . The intensity of this peak was found to be very weak for the sample obtained by the one-step process. The molecular weight of the homo-oligoesters of MG in the two-step kneading shifted to high molecular weight when compared to that of one-step kneading (Fig. 4). These results confirm the above discussion, and lead to the conclusion that a two-step kneading process effectively

improved the grafting and homo-oligoesterification reactions within a relatively short period.

One of the problems of the plasticization of CDA through the melt processing with MAH and Gly is hydrophilicity of the MG-plasticized products. We can expect, however, that the extraction of the plasticizers into water from the products obtained by the two-step kneading should be lower than that for the one-step kneaded products, as oligoesterification is enhanced. As shown in Figure 5, the extraction of plasticizers from the products could be restricted by the two-step kneading process compared with that for one-step kneading process. This result indicates that water-resistant capacity, considered as one of the

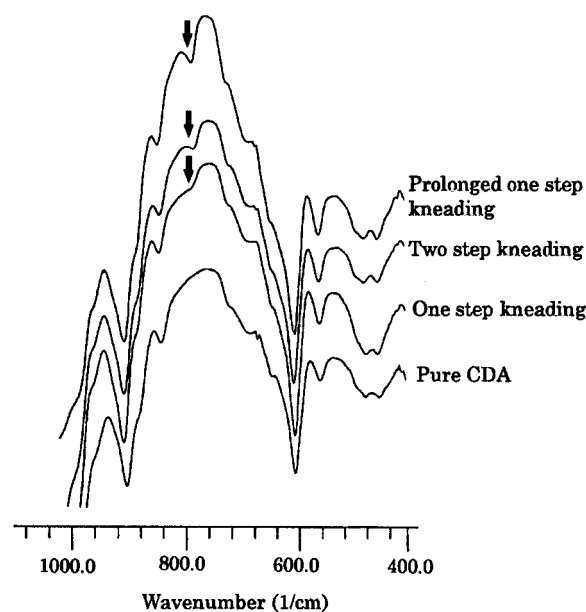


Figure 3 FTIR spectra of CDA plasticized by different kneading methods. Composition of CDA and plasticizers is 75/10/15 (CDA/ATEC/MG).

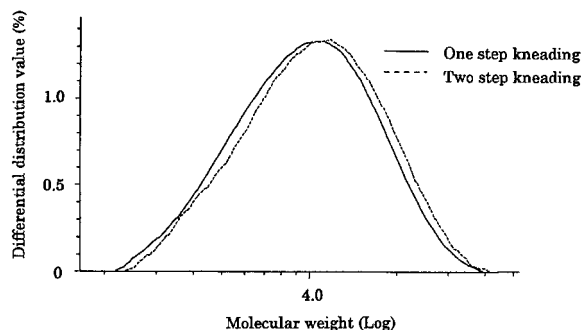


Figure 4 GPC chromatogram of homooligomers of MAH and Gly in the plasticized CDA. Composition of CDA and plasticizers is 75/10/15 (CDA/A TEC/MG).

defects for MG-plasticized CDA, can be improved by this two-step kneading process.

Thermal Properties

The thermal properties of the related plasticized CDA were investigated by means of differential scanning calorimeter (DSC). The results are shown in Table V. Cellulose diacetate, a partially crystalline polymer, used as a reference, showed its melting point at around 230°C, and the T_g at 192.1°C. However, the plasticized CDA showed no melting peak during the first and second scans, indicating that it is amorphous polymer, and the

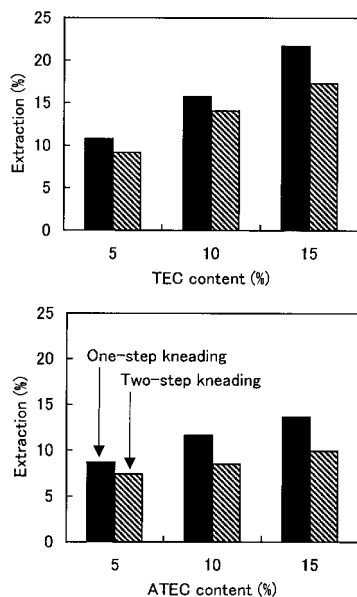


Figure 5 Effects of kneading methods for plasticization of CDA on the extraction of plasticizers into water. Composition of CDA and plasticizers is 75/10/15 (CDA/TEC or ATEC/MG).

Table V DSC Results of CDA Plasticized with MAH, Gly, Citrate Esters, and Their Combinations

Composition (%)	Glass Transition Temperature (T_g , °C)	Melting Temperature (T_m , °C)
Pure CDA	192.1	229.8
25MG	96.3	N. O.
25TEC	99.6	N. O.
25ATEC	112.1	N. O.
15MG/10TEC	89.0	N. O.
15MG/10ATEC	98.5	N. O.

N. O.; Not obtainable.

T_g values (second scan) for all of the plasticized CDA showed a decrease of at least 80°C compared to pure CDA.

CONCLUSIONS

Cellulose diacetate (CDA) was successfully plasticized by melt-processing reaction of CDA with MAH, Gly, and citrate esters, showing the decreases of 80–100°C in the glass transition temperature (T_g) of CDA. Stiff and brittle properties of MAH and Gly (MG)-plasticized CDA were improved by adding the citrate esters as coplasticizers. The mechanical properties of plasticized CDA were comparable to those of general synthetic polymers or commercially plasticized cellulose acetate. The grafting of MG oligoesters to the free hydroxyl groups in CDA and their homo-oligomerization were accelerated by two-step kneading process, and verified by FTIR and GPC measurements. The extraction of plasticizers was also restricted by the two-step kneading process.

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