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BIODEGRADABILITY OF CELLULOSE ACETATE PLASTICIZED WITH CITRATE ESTERS

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ABSTRACT

Cellulose acetate (CA) was melt compounded with two different citric acid esters: triethyl citrate and acetyl triethyl citrate. It was observed, based on the glass transition temperatures, that both plasticizers were miscible with CA. The addition of plasticizer reduced the tensile modulus and increased the elongation of CA. The biodegradation rates increased dramatically with an increase in plasticizer content.

INTRODUCTION

Citrate esters are renewable resource derivatives derived from citric acid, a tribasic monohydroxy acid (2-hydroxy-1,2,3-propanetricarboxylic acid), $C_6H_8O_7$, and a natural constituent and common metabolite of plants and animals. Since citrate esters are derivatives of natural formulations, it is of interest to determine their effect on the biodegradation and plasticization of biodegradable polymers and particularly other renewable resource derivatives such as cellulose acetate (CA). Plasticizers are widely used in the plastics industry to increase the processibility, flexibility, and ductility of polymeric materials. The miscibility of various commercial polymers has been determined using citrate esters as plasticizers [1]. Additional work was performed on using different plasticizers with poly(3-hydroxybutyrate) (PHB) [2] and CA [3]. However, their effects on biodegradation have not been reported. We recently conducted an elaborate study on the compatibility and degradation of PHB [4] and poly(lactic acid) [5] containing varying amounts of citrate esters as plasticizers. Buchanan et al. [6, 7] carried out detailed degradation studies on CA films. In the present work the miscibility and degradability of CA was determined with two different plasticizers based on citrate esters, triethyl citrate (C-2) and acetyl triethyl citrate (A-2).

EXPERIMENTAL

Cellulose acetate with a degree of substitution (DS) of 2.5 and a molecular weight of 30,000 was supplied by Eastman Chemical Company, Kingsport, TN. The citrate esters used in the study were supplied by Morflex Inc., Greensboro, NC.

The compounding of the formulations containing varying amounts of plasticizer was conducted by melt extrusion. A ¾″ single screw extruder (Brabender Inc.) with an L:D ratio of 20:1 was used with a breaker plate and screen pack to improve the mixing of the formulations. A ⅛″ strand die, followed by cooling bath, puller, and pelletizer, was also used for all experiments. Tensile samples were prepared according to ASTM D1708 (CSI Instruments), and the composting samples for the biodegradation test were prepared on a 20-ton Negri-Bossi injection molding machine. Since it was not possible to extrude the CA without a plasticizer, solvent-cast films of CA were prepared from a 20% (w/v) solution in acetone using a Gardner knife. These films were used as a reference for the composting of plasticized CA.

A DuPont DSC 920 was used for the thermal analysis of the formulations. First run DSC scans were carried out at 10°C/min from room temperature. The samples were then quenched using liquid nitrogen to −100°C, and the samples were reheated for a second run at the 10°C/min rate. Glass transition temperatures (T_g) were determined from the second scans.

Tensile testing was carried out on an Instron 3700 at a crosshead speed of 2 in./min following the ASTM D 638. Mechanical properties for all formulations were calculated from the load-elongation curves.

Composting samples were prepared by cutting the injection-molded samples into 1″ × 0.5″ × 0.02″ dimensions. The samples were weighed precisely and then put into a municipal solid waste mixture which consisted of leaves, paper waste, cow manure, food waste, composting seeds, urea, wood waste, and water. The mixture was kept in an oven at 55°C at which the maximum growth of thermophilic microorganisms occurred. The samples were vacuum dried for 24 hours at 45°C and weighed to the nearest 0.1 mg initially and after each measurement. Weight loss of the samples was expressed in $\mu g/mm^2$. A complete description of the laboratoryscale composing test method used in this study was described in detail in an earlier paper [8].

HPLC analysis was carried out on plasticized CA samples before and after degradation in order to determine the concentration of plasticizers. This analysis was carried out at Morflex Inc.

RESULTS AND DISCUSSION

Cellulose acetate, a partially crystalline polymer, shows a melting point at 230°C in the first DSC scan of the as-received powder sample. The T_g of the same sample was observed at 190°C. The CA showed no evidence of a melting peak during the second DSC run, indicating that it was amorphous. The T_g values of the CA blends containing different amounts of citrate esters were determined from the second DSC scans of the extruded pellets and are summarized in Table 1. The T_g of the pure CA (190°C) dropped to about 121 and 120°C with 30 phr of C-2 and A-2, respectively. It is important to note that CA formulations with 40 and 50 phr of the plasticizers did not exhibit clear T_g values (~112–115°C) in the DSC scans. It can be concluded from the depression of the T_g values that C-2 and A-2 are miscible with CA in all compositions.

Figures 1 and 2 show the stress–strain curves of CA containing different amounts (0 to 20 phr) of C-2 and A-2, respectively. It is observed that the tensile modulus and tensile strength at yield decreases while the elongation values increase with an increase in the plasticizer content. It can be seen from the figures that both plasticizers are equally effective in influencing the mechanical properties of CA.

Figures 3 and 4 illustrate the progressive biodegradation of CA with C-2 and A-2, respectively. The biodegradation was measured on 0.020″ thick injection-molded 0.5″ × 1.0″ size samples, and the weight loss measurements were taken at intervals of 7, 14, 21, and 30 days. It can be seen that the biodegradation rate

TABLE 1. DSC Results of Cellulose Acetate with C-2 and A-2

Cellulose acetate formulations[a]	Glass transition temperature, T_g, °C	Melting temperature, T_m, °C
Cellulose acetate (CA)	190	223.5
CA/20 C-2	137	Not observed
CA/30 C-2	121	Not observed
CA/40 C-2	115	Not observed
CA/50 C-2	112	Not observed
CA/20 A-2	138	Not observed
CA/30 A-2	120	Not observed
CA/40 A-2	116	Not observed
CA/50 A-2	113	Not observed

[a] Compositions are in phr of CA.

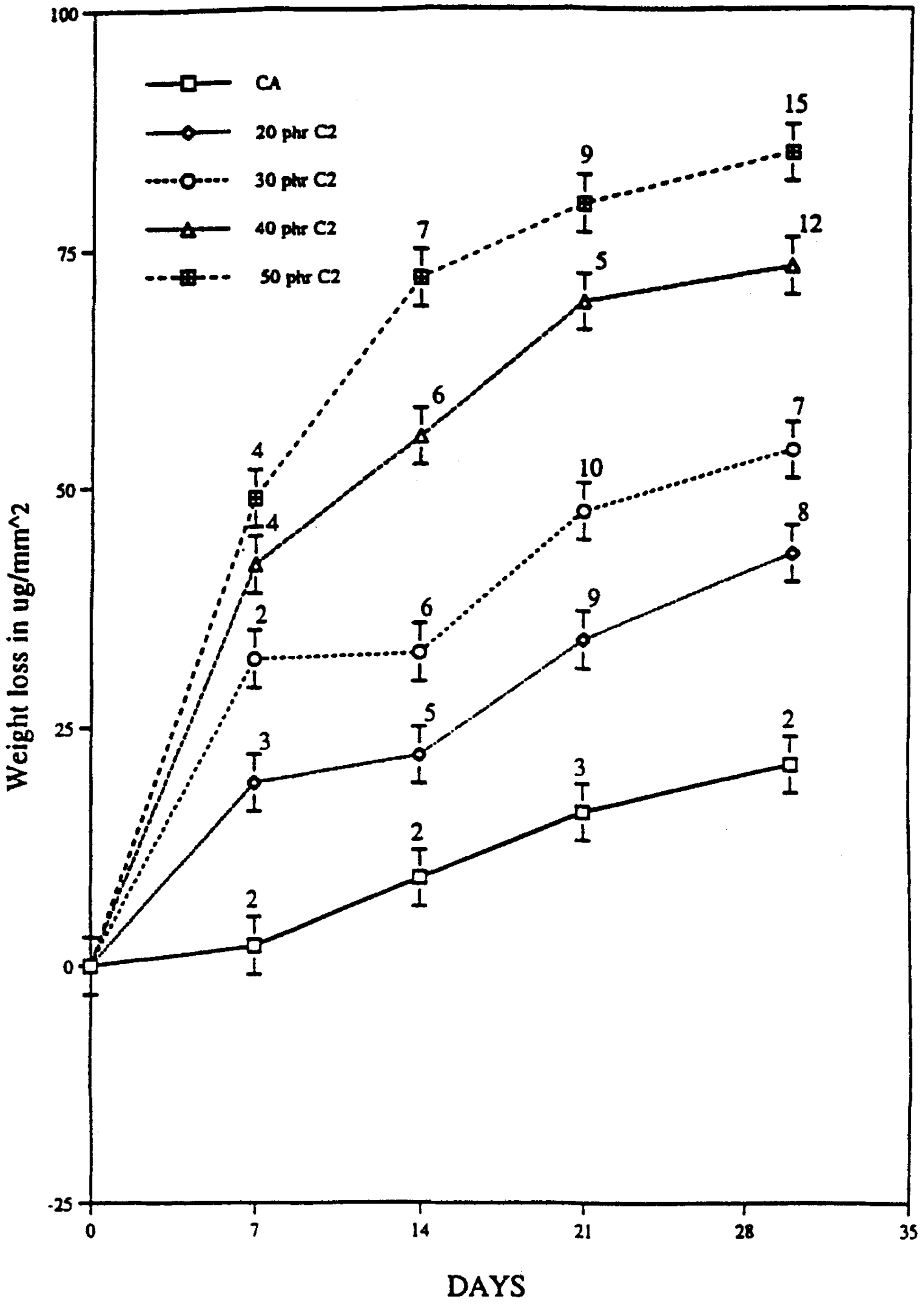

FIG. 1. Stress-strain curves of cellulose acetate with different amounts of C-2.

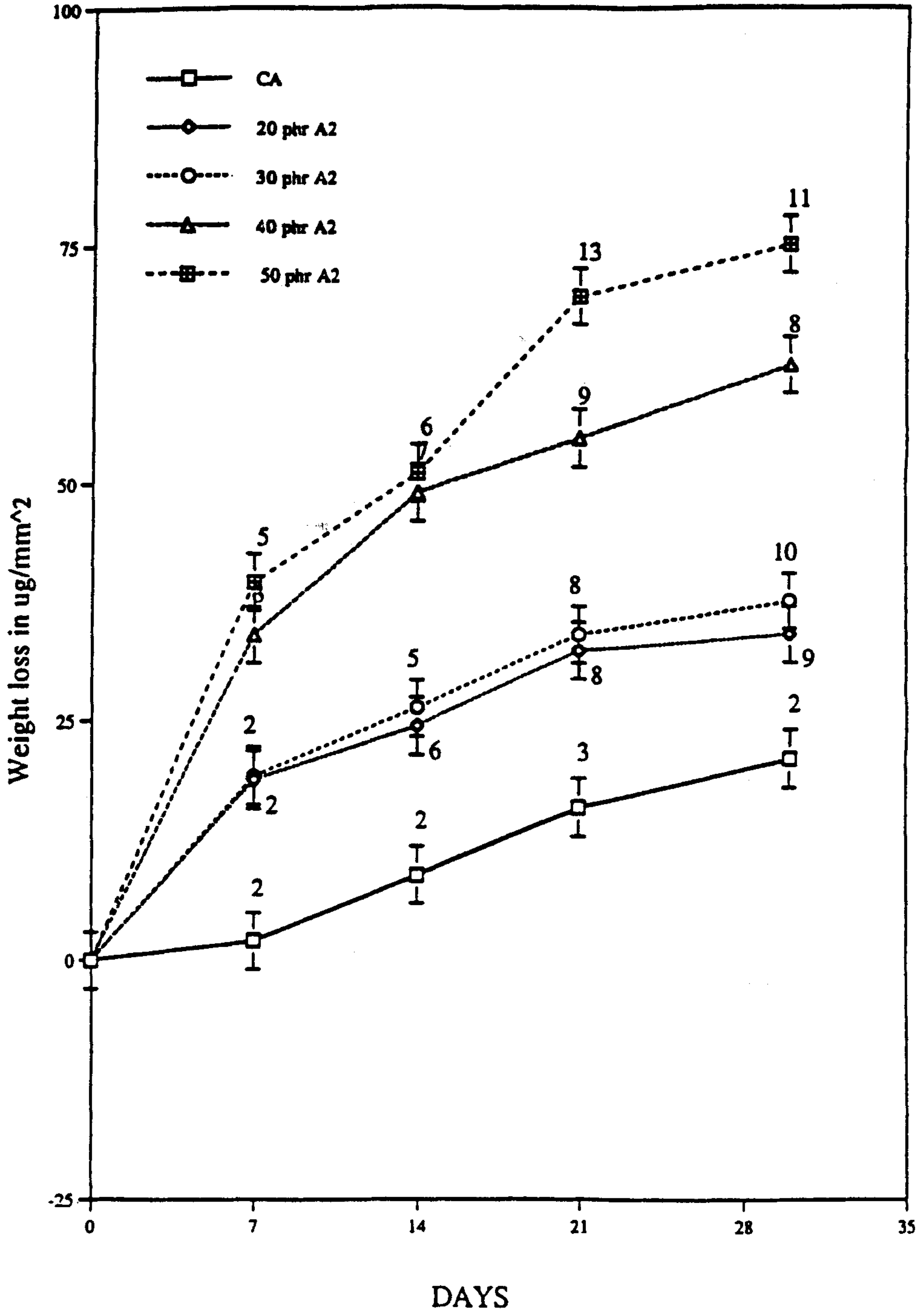

FIG. 2. Stress-strain curves of cellulose acetate with different amounts of A-2.

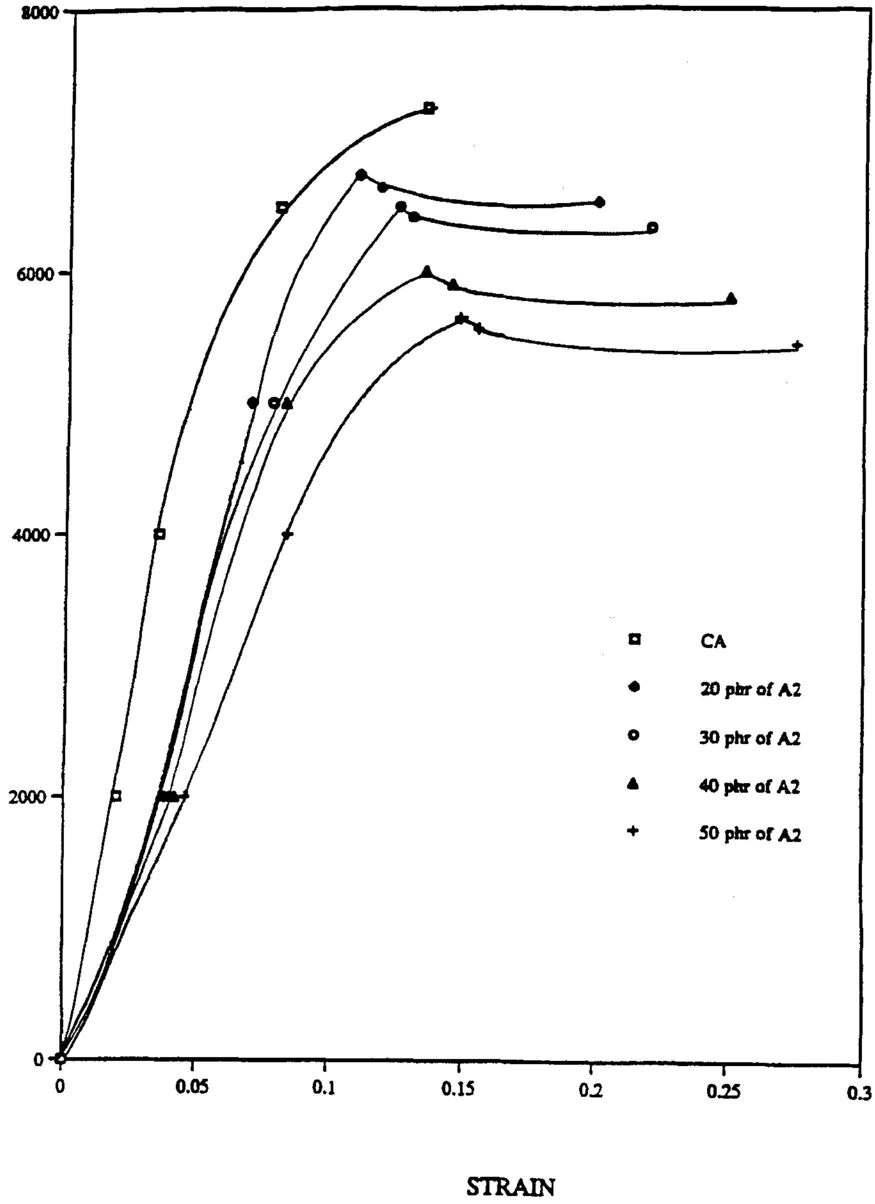

FIG. 3. Progressive biodegradation of cellulose acetate with different amounts of C-2 as a function of time.

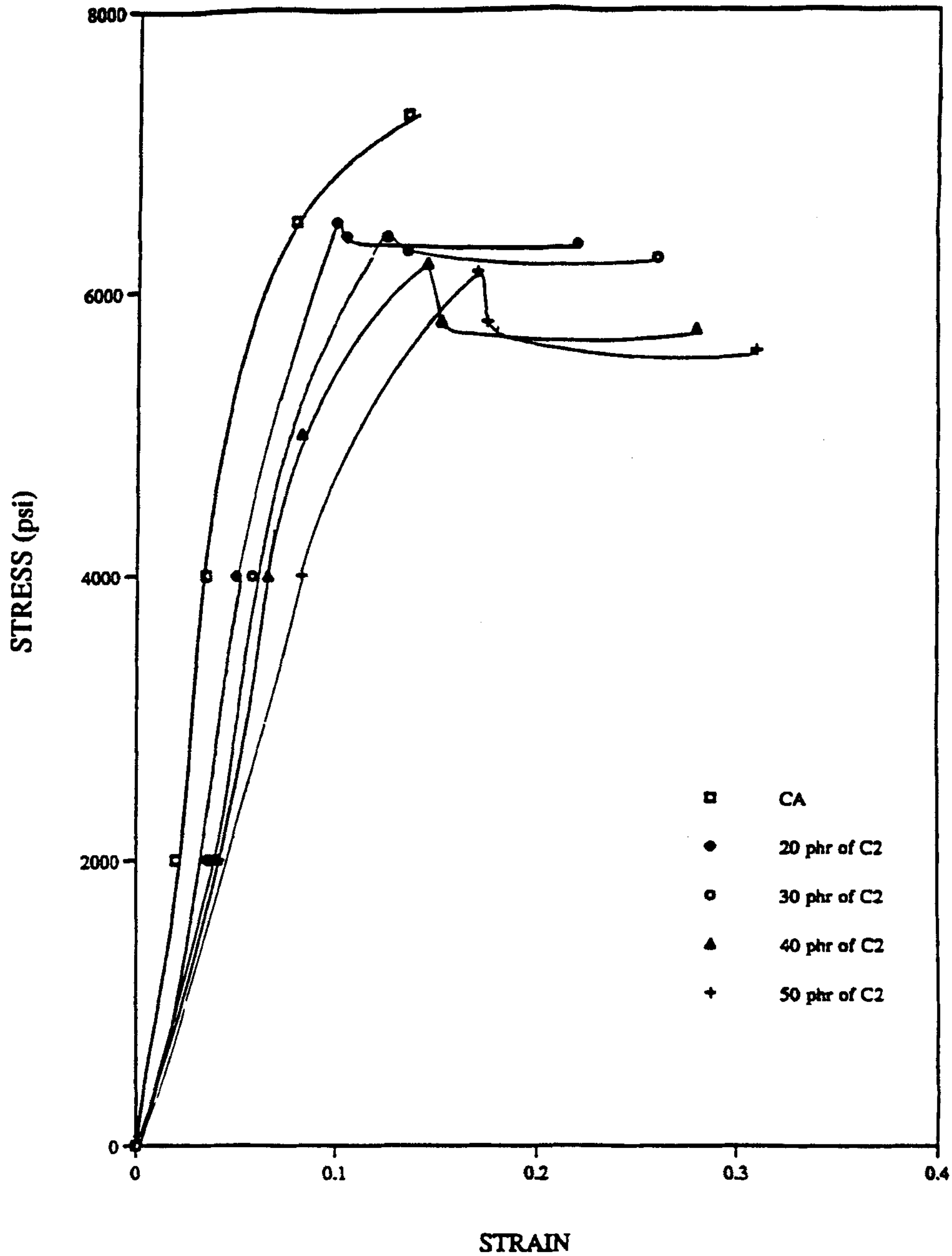

FIG. 4. Progressive biodegradation of cellulose acetate with different amounts of A-2 as a function of time.

TABLE 2. Plasticizer Content of CA/C-2 Compositions by HPLC

(a) Before Degradation

PHR (%)	C-2 (%)	TEA (%)
20 (16.7)	16.7	0.02
30 (23.1)	22.7	0.020
40 (28.6)	26.74	0.026
50 (33.4)	28.88	0.025

(b) After Degradation

PHR (%)	Days	C-2 (%)	TEA (%)
20 (16.7)	7	12.6	0.01
	14	6.7	0.01
	21	4.7	0.01
	30	2.6	0.00
30 (23.1)	7	10.3	0.01
	14	11.3	0.01
	21	5.8	0.00
	30	4.8	0.00
40 (28.6)	7	10.3	0.01
	14	9.2	0.06
	21	5.83	0.00
(Control)	21	7.0	0.01
	30	2.8	0.00
50 (33.4)	7	13.9	0.01
	14	13.1	0.04
	21	5.4	0.00
	30	3.6	0.01

(c) Normalized Weight Loss of CA in the CA/C-2 Compositions

Plasticizer content before degradation (%)	Time (days)	Total weight loss during composting (μg/mm^2)	Plasticizer loss during composting (%)	Normalized weight loss of CA (μg/mm^2)
16.7	7	18.74	4.1	17.97
	14	22.8	10.0	20.52
	21	33.3	12.0	29.30
	30	41.7	14.1	35.82
22.7	7	31.2	12.4	27.33
	14	31.2	11.4	27.64
	21	46.8	16.9	38.89
	30	52.1	17.9	42.77
26.74	7	41.6	16.44	34.76
	14	54.1	17.54	44.61
	21	68.7	20.91	54.33
	30	70.8	23.94	53.85
28.88	7	48.83	14.98	41.51
	14	71.2	15.78	59.96
	21	79.2	23.48	60.6
	30	85.4	25.28	63.81

TABLE 3. Plasticizer Content of CA/A-2 Compositions by HPLC

(a) Before Degradation

PHR (%)	A-2 (%)	C-2 (%)	TEA (%)
20 (16.7)	16.14	0.15	0.17
30 (23.1)	20.90	0.75	0.17
40 (28.6)	23.38	5.40	0.11
50 (33.4)	29.24	0.15	0.13

(b) After Degradation

PHR (%)	Days	A-2 (%)	C-2 (%)	TEA (%)
20 (16.7)	7	12.35	0.4	0.41
	14	11.28	0.6	0.41
	21	8.64	0.4	0.49
	30	5.47	0.9	0.31
30 (23.1)	7	16.25	0.7	0.39
	14	16.88	0.6	0.30
	21	13.43	1.1	0.34
	30	8.43	1.0	0.42
40 (28.6)	7	19.27	2.4	0.22
	14	16.68	1.6	0.23
	21	13.34	0.9	0.32
(Control)	21	16.57	0.9	0.47
	30	11.59	0.8	0.42
50 (33.4)	7	14.00	3.0	0.25
	14	11.23	1.2	0.21

(c) Normalized Weight Loss of CA in the CA/A-2 Compositions

Plasticizer content before degradation (%)	Time (days)	Total weight loss during composting (μg/mm2)	Plasticizer loss during composting (%)	Normalized weight loss of CA ($\mu g/mm^2$)
16.14	7	16.7	3.79	16.06
	14	20.8	4.86	19.78
	21	29.2	7.50	27.01
	30	31.0	10.67	27.69
20.9	7	16.7	4.65	15.92
	14	25.0	4.02	23.99
	21	33.3	7.47	30.81
	30	37.5	12.47	32.82
23.38	7	33.3	4.11	31.93
	14	47.9	6.7	44.68
	21	54.2	10.04	48.75
	30	60.4	11.79	53.27
29.24	7	39.6	15.24	33.56
	14	51.2	18.01	41.97

increases with an increase in the plasticizer content (from 20 to 50 phr) for C-2 and A-2. It is observed that the degradation of CA/C-2 formulations is higher than the CA/A-2 formulations.

Tables 2 and 3 summarize the amount of plasticizer in the CA formulations as determined by HPLC. The analyses were carried out to determine the concentration of C-2, A-2, and triethyl aconiatate (TEA) in the formulations after processing (i.e., before degradation) and after degradation. The results obtained for the plasticizer content before degradation for all the formulations are reasonable values [Tables 2(a) and 3(a)]. The observed loss in the plasticizer content before composting is due to degradation of the plasticizer during processing (decomposition temperatures for C-2 and A-2 are 168 and 172°C, respectively). The percent plasticizer content after degradation for different time periods (7 to 30 days) for the formulations are summarized in Tables 2(b) and 3(b). The plasticizer content in the samples

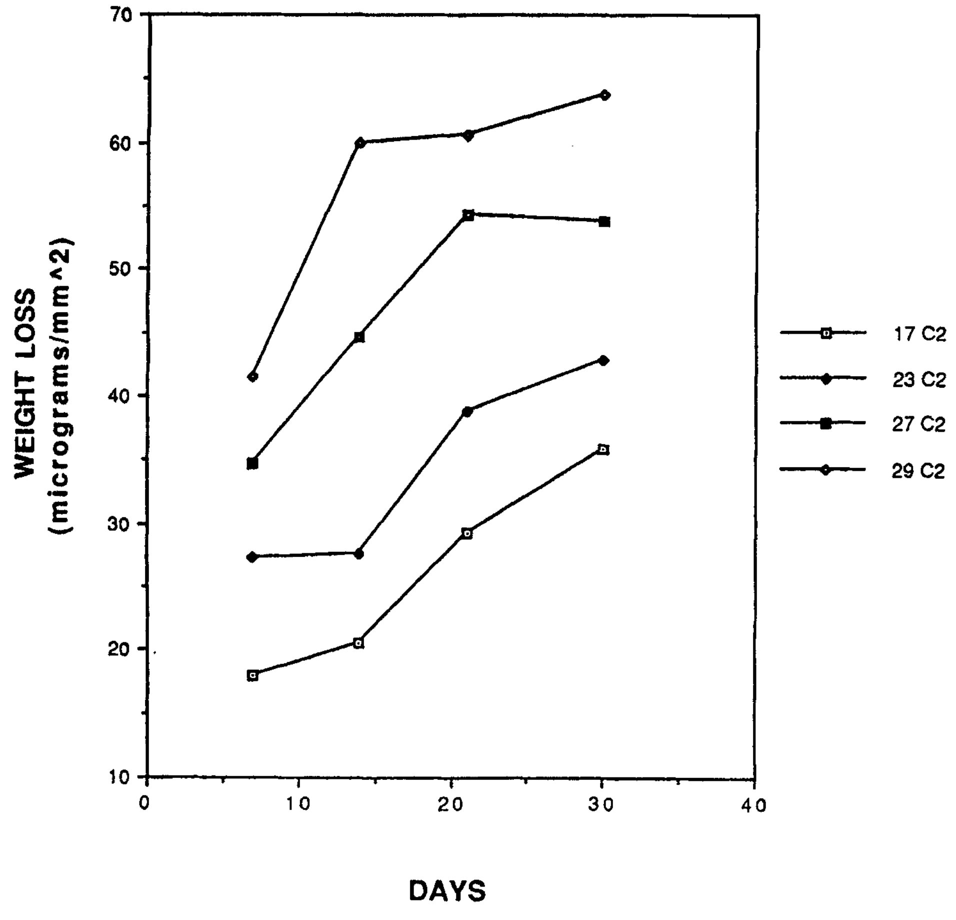

FIG. 5 Normalized weight loss of cellulose acetate with different amounts of C-2 as a function of time.

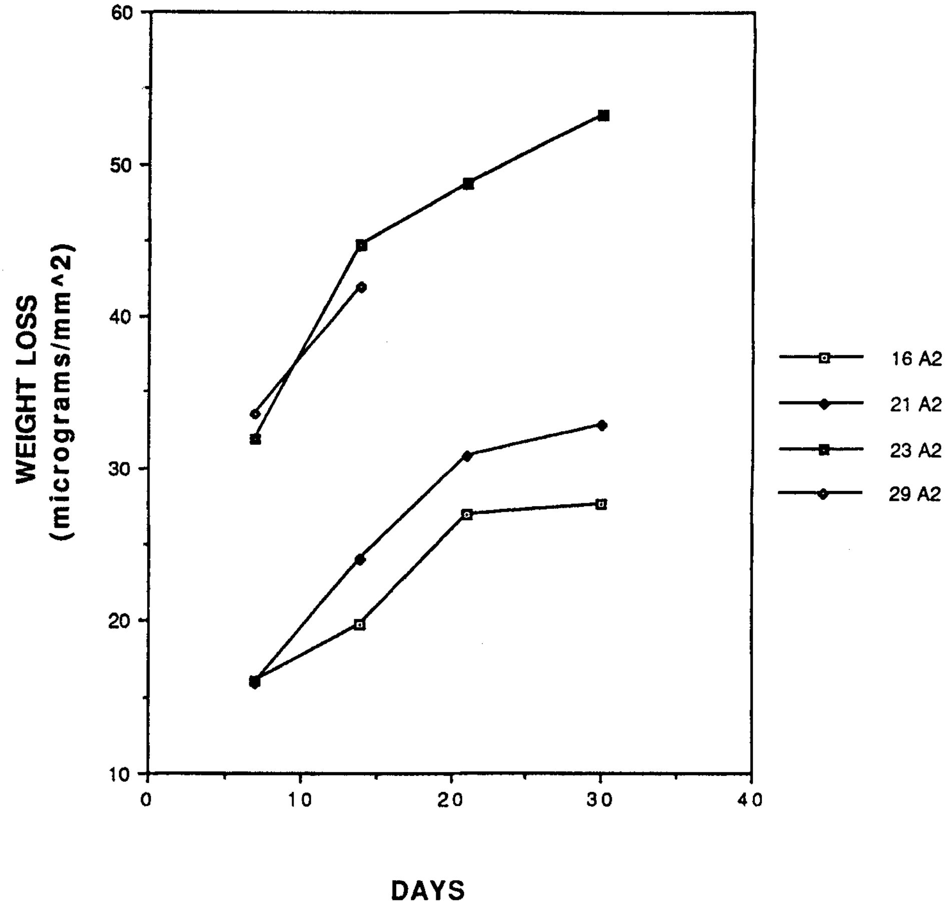

FIG. 6. Normalized weight loss of cellulose acetate with different amounts of A-2 as a function of time.

retrieved from the composting reactors decreases with increasing time of degradation. This indicates that the plasticizers are dissolving or degrading during the composting cycle. The plasticizer content in the control reactors also decreased due to dissolution or hydrolysis of the plasticizers.

The amount of plasticizer remaining in the samples after degradation was utilized to calculate the normalized weight loss due only to CA. The plasticizer loss during composting was determined by the difference in the plasticizer content before and after degradation [column 4 in Tables 2(c) and 3(c)]. The normalized weight loss of cellulose acetate was obtained by subtracting the plasticizer loss from the total weight loss during composting. Figures 5 and 6 shows the normalized weight loss of only CA acetate for different amounts of C-2 and A-2 as a function of degradation time, respectively. The figures demonstrate that there is an increase in the weight loss of CA with an increasing amount of plasticizer content.

CONCLUSIONS

The depression of the glass transition temperature of CA formulations with C-2 and A-2 confirms that the plasticizers are miscible with CA. These plasticizers allow very good processibility of cellulose acetate with typical mechanical properties of plasticized CA.

The composting studies show a dramatic increase in the rate of weight loss of plasticized CA with increasing amounts of citrate esters. HPLC results indicate that the degradation of CA is accelerated due to the citrate esters, resulting in a synergistic effect.

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