

Citrate Esters as Plasticizers for Poly(lactic acid)

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ABSTRACT: Citrate esters were used as plasticizers with poly(lactic acid) (PLA). Films were extruded using a single-screw extruder with plasticizer contents of 10, 20, and 30% by weight. All of the citrate esters investigated were found to be effective in reducing the glass transition temperature and improving the elongation at break. It was observed that the plasticizing efficiency was higher for the intermediate-molecular-weight plasticizers. Hydrolytic and enzymatic degradation tests were conducted on these films. It was found that the lower-molecular-weight citrates increased the enzymatic degradation rate of PLA and the higher-molecular-weight citrates decreased the degradation rate as compared with that of unplasticized PLA. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 1507–1513, 1997

Key words: citrate esters; poly(lactic acid); plasticizers; biodegradation; films

INTRODUCTION

Poly(lactic acid) (PLA) is a biodegradable thermoplastic which is biocompatible, ecologically safe, and commercially produced from renewable resources. PLA and its copolymers are used primarily in a number of medical applications such as sutures, drug delivery, orthopedic implants, etc.¹ It possesses good mechanical properties and clarity in addition to its processability,^{2,3} however its brittleness is its major drawback for many applications. In order to modify various properties, PLA has been blended with other polymers such as poly(glycolic acid),⁴ poly(ethylene vinyl acetate),⁵ poly(ϵ -caprolactone),⁶ poly(ethylene oxide/propylene oxide–ethylene oxide) triblock copolymer,⁷ poly(vinyl acetate),⁸ and poly(ethylene oxide).⁹

In this investigation, an effort has been made to study the use of citrate esters as plasticizers with PLA and their effect on the thermal and mechanical properties and degradation behavior. Citrate plasticizers are derived from naturally occurring citric acid. They are nontoxic, have been approved for many applications (such as additives in medical plastics, personal care, and food contact)¹⁰ and are used as plasticizers with a variety of different polymers.¹¹ Cellulose acetates plasticized with citrate esters were found to possess improved processability and accelerated degradation rates in the composting environment.¹²

Plasticizers strongly influence the glass transition temperature (T_g) and crystallinity of a polymer. The objective of the present investigation is to study the effects of a series of citrate esters on the physical properties of PLA and subsequently the degradation behavior.

EXPERIMENTAL

Materials

PLA (grade: DVD 439-451-4) was supplied by Cargill Inc. (EcoPla Division, Minnesota) with a

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Table I Properties of Citrate Esters¹⁰

Name	Code	Molecular Weight	Density (g/mL)	Boiling Point at 133 Pa (°C)	Solubility in Water (g/100 mL)	Solubility Parameter ^a (J/cm ³) ^{1/2}
Triethyl citrate	C2	276	1.136	126	6.5	19.8
Tributyl citrate	C4	360	1.104	169	< 0.1	18.8
Acetyl triethyl citrate	A2	318	1.135	131	0.72	19.6
Acetyl tributyl citrate	A4	402	1.046	173	< 0.1	18.7

^a Calculated.

molecular weight (M_w) of 137,000. The plasticizers were provided by Morflex Inc., North Carolina. The properties of the plasticizers used are listed in Table I.

Methods

Film Extrusion

The polymer was first dried in a vacuum oven at 40°C overnight, and then 10% of the plasticizer was mixed with the granules physically for 20 min. This mixture was extruded on a single-screw extruder (C. W. Brabender) with an L/D of 20 and screw diameter of .75 in. The extrudates were quenched with water and pelletized. Compositions containing 10% plasticizer were physically mixed with an additional 10 and 20% plasticizer for 10 min. to achieve the 20 and 30% compositions, and these mixtures were allowed to stand overnight. These mixtures and the neat PLA were extruded on a single-screw extruder with a film die. The processing conditions were: Zone 1, 130°C; Zone 2, 140°C; Zone 3, 150°C; Adaptor, 155°C; Die, 160°C; and RPM, 20.

The film was extruded vertically downward and drawn by chilled rolls. The thickness of the film was adjusted to 20 μm by controlling the takeup speed.

Neat PLA was also subjected to the identical two processing cycles to ensure that the thermal histories were the same. Compositions containing 30% C4 or A4 could not be processed due to feed and conveyance problems.

Thermal Analysis

A TA Instruments differential scanning calorimeter (Model 9900) was used for the thermal characterization of the samples. All of the scans were

conducted at a heating rate of 10°C/min between -75 and 180°C under a nitrogen atmosphere using approximately 10 mg of sample. T_g s, melting points, and enthalpies of fusion were measured.

Tensile Testing

Tensile testing was carried out on an Instron tensile testing machine (Model 1137) as per ASTM D882-90. The testing was performed in the machine direction, using a gauge length of 10 cm and sample width of 2.5 cm with a crosshead speed of 5 cm/min. An average of five test values were taken for each sample. The standard deviation was found to be within 5% for tensile strength and 10% for elongation at break.

Hydrolytic Degradation

Films having an approximate thickness of 20 μm and measuring 2.5 cm \times 2.5 cm were weighed and

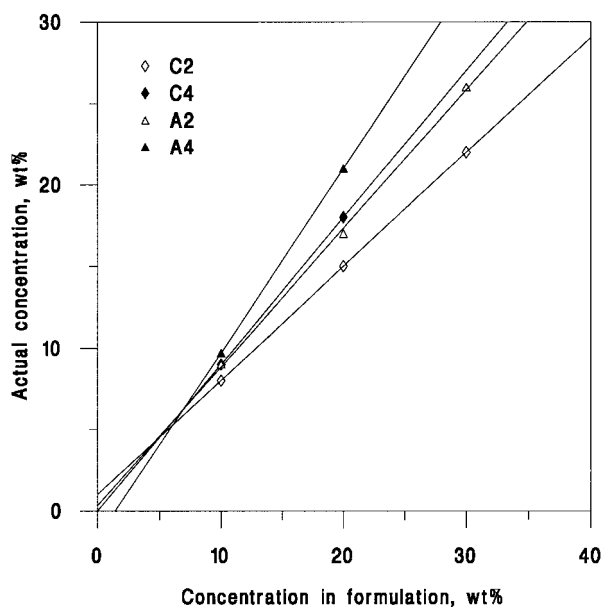


Figure 1 Plasticizer concentration in film plotted against the concentration added in formulation.

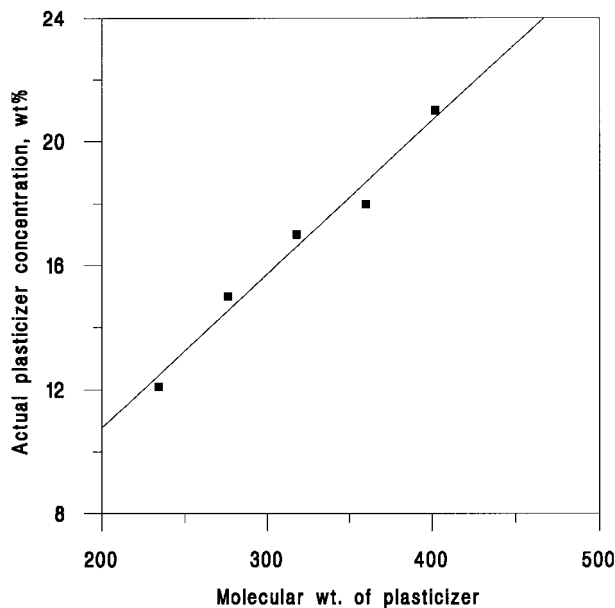


Figure 2 Plasticizer concentration in film plotted against the molecular weight of the plasticizers for 20% added concentration.

placed in glass vials containing 18 mL of 0.05 M NaHCO_3 /0.10 molar NaOH having a pH of 10.6. The test was carried out at 37°C in a rotary shaker maintained at 100 rpm. Three replicate films in separate vials were removed at specified times. The samples were washed with distilled water, dried in a vacuum oven at room temperature for 48 h, and weighed. The standard deviation for these values was 3 to 5%.

The rate of hydrolysis of the pure plasticizers under similar conditions was also measured. One gram of plasticizer was added to 18 mL of the buffer solution and the pH change with time was recorded.

Enzymatic Degradation

A stock of enzyme solution was prepared having a pH of 8.6 with Tris/HCl buffer containing sodium azide and the enzyme Proteinase K, both 200 mg/L. Accurately weighed samples measuring 1 cm \times 1 cm were placed into glass vials and 5 mL of the enzyme solution was added. The controls were also conducted without the enzyme. The degradation study was carried out in a rotary shaker at 37°C and 200 rpm. Three replicates of each sample were removed at specified time intervals (filtered if disintegrated into small pieces), washed with water, dried in a vacuum oven at room temperature for 48 h, and weighed. The pure plasti-

cizers were also subjected to similar conditions, both with and without enzyme, and the change in pH was measured.

RESULTS AND DISCUSSION

The properties of the citrate plasticizers used in this study are shown in Table I. It can be seen that molecular weight has a strong influence on all of the properties, particularly density, stability, and solubility in water. As the molecular weight increases, the molecule becomes less polar—as indicated by both water solubility and solubility parameter—and the boiling point increases.

The extruded samples were subjected to HPLC to determine the concentration of the plasticizers in the films. The concentration values obtained from HPLC results for each systems were plotted against the percentage that was added originally in the formulation (Fig. 1). It can be seen that the actual concentration is decreased due to evaporation loss during processing. The extent of loss increases linearly with increasing original concentration, and the slopes connecting these points increase with increasing M_w corresponding to a decreasing loss. In Figure 2 the remaining concentration values of plasticizers for the original 20% content are plotted against their molecular

Table II Thermal and Mechanical Properties of PLA Plasticized with Different Citrate Esters

	T_g (°C)	T_m (°C)	ΔH (J/g)	Tensile Strength (MPa, yield)	Elongation at Break (%)
PLA	59.1	145.2	0.79	51.7	7
C2					
10	42.1	134.1	0.31	28.1	21.3
20	32.6	130.9	2.86	12.6	382
30	22.0	126.8	7.57	7.2	610
C4					
10	40.4	143.1	0.06	22.4	6.2
20	17.6	139.0	19.1	7.1	350
A2					
10	50.8	141.7	0.91	34.5	10
20	30.0	138.1	0.91	9.6	320
30	14.2	131.6	18.34	7.6	228
A4					
10	25.4	139.2	1.4	17.7	2.3
20	17.0	138.9	3.9	9.2	420

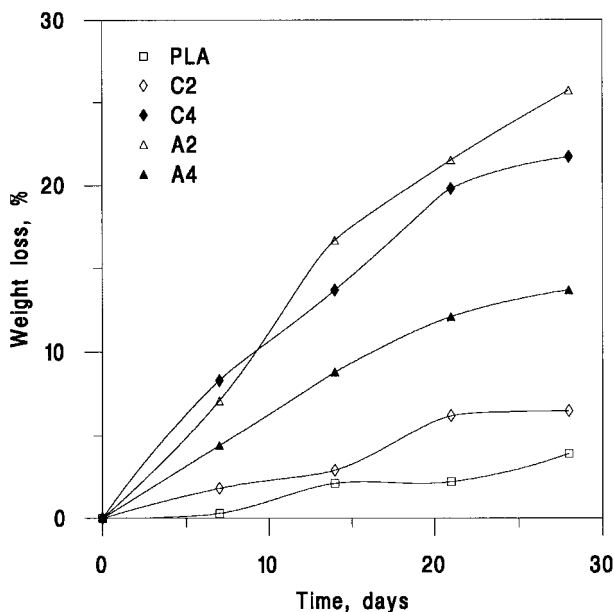


Figure 3 Weight loss for neat PLA and different samples with 20% plasticizer concentration plotted against time during hydrolytic degradation.

weights. Here also, a linear relationship can be observed. The loss during processing is directly proportional to the original concentration and inversely proportional to the M_w .

Differential Scanning Calorimetry

The results obtained from differential scanning calorimetry are shown in Table II. All of the compositions show a single T_g which is lower than that of the neat PLA. The maximum depression of T_g was as much as 45°C for the concentration range studied. All of the plasticizers evaluated were miscible with PLA.

A significant depression of the crystalline melting point (up to 15°C) was also observed and found to increase with an increase in plasticizer content, as is a typical behavior for plasticized semicrystalline polymers. The heat of fusion (ΔH_f) values were found to increase as the plasticizers were added, as compared with the neat PLA which had a ΔH_f of 0.8 J/g. (ΔH_f for 100% crystalline PLA is 93 J/g¹³). Compositions containing plasticizers had ΔH_f values up to 19 J/g, corresponding to a crystallinity of ~ 20%. This increase in crystallinity is due to the depression of the T_g below room temperature, which allows crystallization to occur during storage.¹⁴ Naturally functionalized oils have been found to improve the crystallization behavior of poly(ethylene tereph-

thalate).¹⁵ Enhanced molecular mobility due to the presence of plasticizer can cause an increase in crystallinity. In the present case of PLA, within the concentration limits studied, all of the plasticizers seem to enhance the crystallinity to some extent.

Mechanical Properties

One of the primary functions of a plasticizer is to improve the elongation at break and toughness, however this has to be achieved at the expense of tensile strength and modulus. Tensile strength at yield and elongation at break for all of the compositions are shown in Table II. As expected, all of the plasticizers decrease the tensile strength of PLA significantly (by ~ 50%) even at 10% concentration, and the deterioration is larger with higher concentrations. On the other hand, elongation at break does not show any significant change at the lower percentages but dramatically increases at the higher concentrations in all cases. A concentration corresponding to the initiation of the glass transition movement is necessary for these high elongations. A maximum value of 610% was observed for C2.

Hydrolytic Degradation

The results of hydrolytic degradation testing conducted at a pH of 10.6 and 37°C for up to 25 days

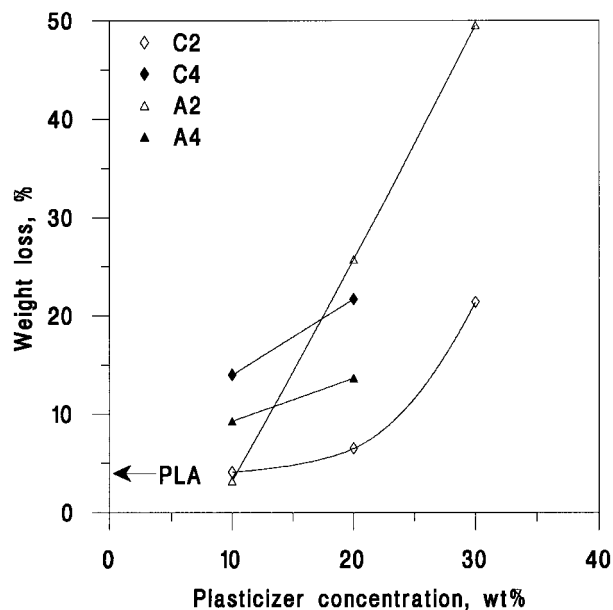


Figure 4 Weight loss values plotted against plasticizer concentration after 28 days of hydrolytic degradation.

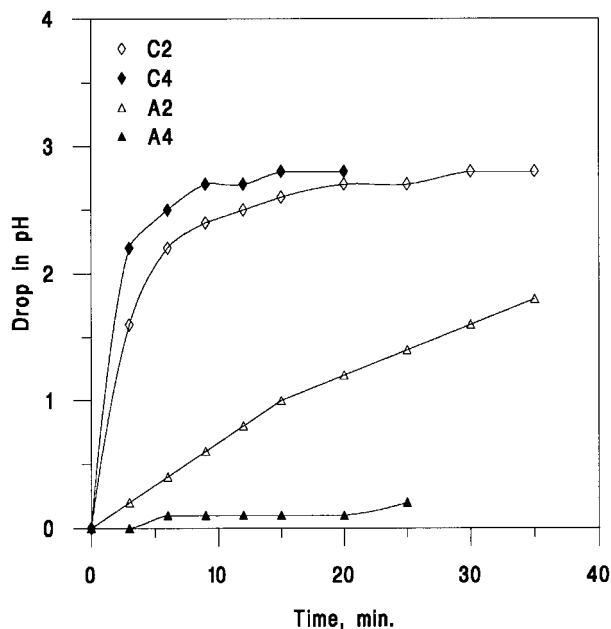


Figure 5 Change in pH plotted against time for different plasticizers under hydrolytic conditions.

are illustrated in Figures 3 and 4. Figure 3 shows weight loss of different samples (20% original concentration) as a function of time as well as that of neat PLA. PLA showed the lowest weight loss (under 5%) after 28 days, whereas all of the other samples showed higher weight losses. Here different factors influence the degradation rate, namely, T_g , crystallinity, and water solubility of the plasticizer in the medium. It is seen that samples with higher water solubility show higher weight losses. If the plasticizer is soluble it diffuses out of the polymer, thereby resulting in a weight loss as well as facilitating faster permeation of the buffer into the polymer. In the cases where the T_g of the composition is lower than the test temperatures (37°C), the weight loss proceeds faster with the polymer in the rubbery state. The compositions containing A2 seem to be an exception, having a high weight loss but a T_g equal to that of C2 and poorer solubility.

The effect of plasticizer concentration on the degradation after 28 days is illustrated in Figure 4. In general there is an increasing extent of weight loss with an increase in concentration, A2 again proving to be an exception. At lower concentrations A2 is below all of the other samples but at higher concentrations, it shows maximum weight loss.

Neat plasticizers were subjected to a similar hydrolysis test and the rate of hydrolysis was measured as a function of change in pH (Fig. 5).

Here the effect of hydrophilicity on the hydrolysis can be clearly seen. The acetylated plasticizers A2 and A4 both showed much lower rates, whereas the unacetylated ones showed higher rates. Both C2 and C4 seem to be highly active until the pH becomes neutral and proceed at a very slow rate thereafter. The highly hydrophobic A4 had the lowest rate of hydrolysis.

Enzymatic Degradation

Enzyme-catalyzed hydrolysis of PLA for drug release application has been reported by Ashley and McGinity.¹⁶ The enzyme Proteinase K has been found to be highly effective in hydrolyzing PLA. Dramatic effects of polymer stereochemistry and the resulting crystalline morphology on enzymatic degradation of poly(β -hydroxybutyrate)¹⁷ and PLA¹⁸ have been investigated in our laboratory. In another study, the effects of crystallinity and orientation of PLA on its enzymatic degradation have also been reported.¹⁹ It was therefore of interest to investigate the effect of plasticizers on the enzymatic degradation behavior of PLA.

The effect of enzyme treatment on the weight loss of different samples (at 20% original concentration) as a function of time are shown in Figure 6. The A2 sample disintegrated completely in 8 h, followed by PLA at 30 h. These specimens were of lower initial crystallinity. Both C2 and A2 are soluble in water, which would also be expected to

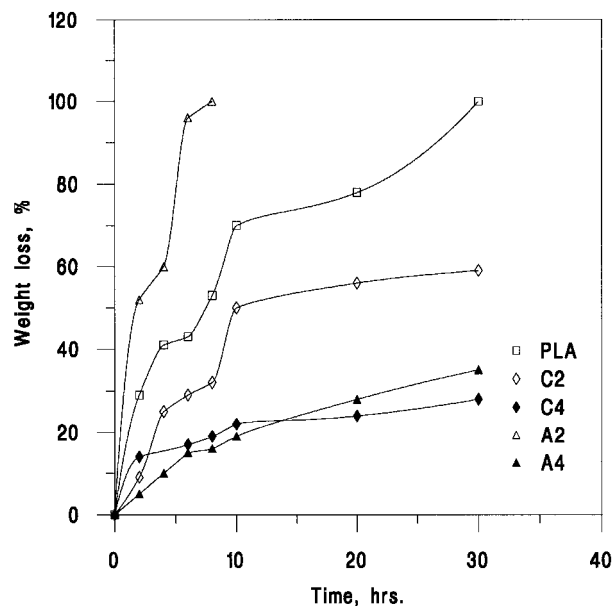


Figure 6 Weight loss values plotted against time for neat PLA and different samples with 20% plasticizer concentration during enzymatic degradation.

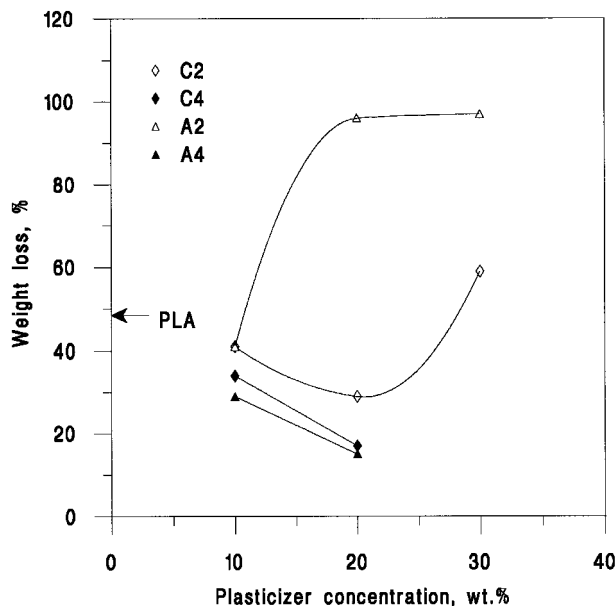


Figure 7 Weight loss values plotted against plasticizer concentration after 6 h of enzymatic degradation.

increase the degradation rate. The samples C4 and A4 had a moderate rate of degradation for the first 10 h and decreased after that. It is possible that since both plasticizers are hydrophobic, they remained in the polymer. Both samples' T_g s are much below the test temperature; hence the crystallinity could have increased, as evidenced by the appearance of these samples which turned from clear to opaque with time. Crystalline regions are more resistant to enzymatic degradation and hydrolysis.^{19,20}

The effect of concentration of plasticizers on the weight loss after 6 h of enzyme exposure is illustrated in Figure 7. For C2 and A2 the trends look somewhat similar to that of hydrolytic degradation, but in the case of C4 and A4, higher concentrations of plasticizer have actually caused a decrease in the extent of degradation. A combination of several factors, such as plasticizer solubility, T_g of the samples, and crystallization, seems to cause this mixed trend. Solubility of plasticizers in the medium (water, in this case) favors degradation. Low T_g initially favors degradation but at the same time facilitates the crystallization of the polymer as time proceeds. Susceptibility of the plasticizers to hydrolysis may also affect the overall rate to some extent. The results obtained from the plasticizer-enzyme exposure test are illustrated in Figure 8 using buffer without (a) and with (b) enzyme. The presence of the enzyme seems to have no effect on the hydrolysis of the plasticizers. The alkaline pH (8.6) caused some

hydrolysis in low molecular weight plasticizers but the high molecular weight plasticizers—namely, C4 and A4—seem to be unaffected even after 15 h. Further studies are necessary to correlate the hydrolyzability of the plasticizers to that of the plasticized compositions.

CONCLUSIONS

All of the plasticizers studied were found to be miscible with PLA at all compositions. Consider-

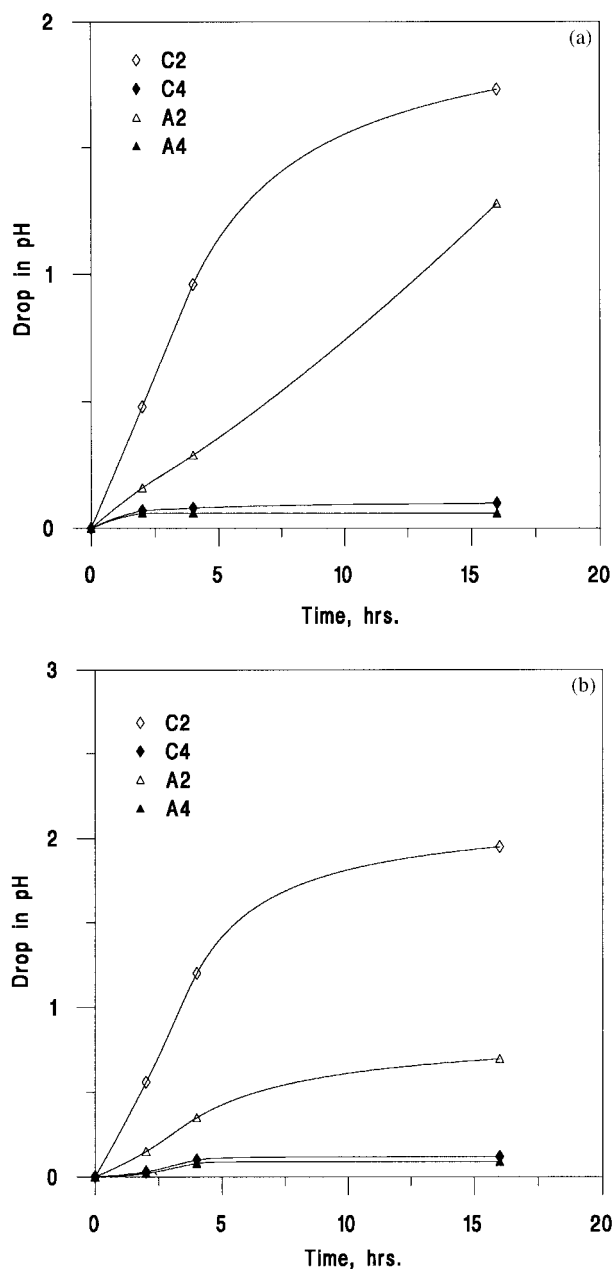


Figure 8 Change in pH values plotted against time for different plasticizers: (a) with buffer; (b) with buffer and enzyme proteinase K.

able loss of plasticizer was observed during processing with the lower-molecular-weight types. A significant improvement in elongation at break values was achieved at the expense of tensile yield strength. Both hydrolytic degradability and enzymatic degradability of the plasticized PLA compositions were influenced by plasticizer solubility, T_g , and crystallinity in a combined manner.

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