Biodegradable Food Packaging.
I. Thermal Stability of Citrus Ester Plasticizers with Role in Polymeric Packaging

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Abstract: This paper presents the thermal analysis with thermogravimetry (TG) techniques of some triesters of citric acid (2-hidroxy-1,2,3 propane tricarboxylic acid) by taking into account aliphatic alcohols from C2-6, iso C10 and iso C13 along with a special alcohol of a complex aliphatic-aromatic structure, namely 2-[(p-nonyl) phenoxy] ethanol. By varying the relationship between these alcohols, two series of products have been realized with role in polymeric packaging. The natural source of the citric acid promotes a presumable and adequate biodegradability potential.

Keywords: unsymmetrical citric triesters, thermal analysis, 2-[(p-nonyl) phenoxy] ethanol.

Abbreviations:

C 2-6.1	di-2-ethyl hexyl 2-(p-nonyl-phenoxy) ethyl citrate
C 2-6.2	2-ethyl hexyl di-2-(p-nonyl-phenoxy) ethyl citrate
C izo 10.1	di-isodecil 2-(p-nonyl-phenoxy) ethyl citrate
C izo 10.2	isodecil di-2-(p-nonyl-phenoxy) ethyl citrate
C izo 13.1	di-isotridecil 2-(p-nonyl-phenoxy) ethyl citrate
C izo 13.2	isotridecil di-2-(p-nonyl-phenoxy) ethyl citrate
C 0.3	tri-2-(p-nonyl-phenoxy) ethyl citrate

1. Introduction

A series of polymer films are used for packaging in food industry, because they are easily and inexpensively produced from uniform raw materials and are flexible as well as durable. The main disadvantage of these films is that they are not biodegradable. The growth of environmental concerns has raised interest in the use of biodegradable alternatives originating from renewable sources [1, 2].

Citric acid with (CA) one hydroxyl and three carboxyl groups exists in citrus fruits and pineapples, where it is the main organic acid. In the research work of Ghanbarzadeh B. et al. [3], citric acid was as the additive chosen for the following reasons. First of all, as a result of its multi-carboxylic structure, interaction could take place between the carboxyl groups of CA and the hydroxyl groups on the starch. Such an interaction would improve the water resistibility due to reducing available OH groups of starch [4]. On the other hand the carboxyl groups of CA can form stronger hydrogen bonds with the hydroxyl groups of starch molecules, so as to prevent recrystallization and retrogradation. Furthermore, because of the multi-carboxyl structure, CA may serve as a cross-linking agent and hence, it may improve the mechanical properties and water resistibility [5]. And as a third point, CA is rated as nutritionally harmless since it is a nontoxic metabolic product of the body (Krebs or citric acid cycle) and it has already been approved by FDA for using in food formulations [6].

Citric esters are produced on an industrial scale and are sold under the name Citroflex and Morflex [7].

Citric esters are also known both as food additives and as additives in cosmetics [8, 9].

Powerful analysis techniques (eg LC / MS) were used to investigate the contamination of food with citric compounds used in lamination of films of poly (vinylidene chloride), cellulose acetate or nitrocellulose coated with regenerated cellulose [10, 11]. The effect of processing food (microwave heating [42] and sterilization by γ-ray irradiation [12]) was also studied on the migration of citric plasticizers films. Thus, there was established a link between migration and heating time, microwave power respectively the initial concentration of plasticizer in the polymer film in question [13]. The effect of gamma irradiation on the migration of citric plasticizers characteristics of PVC films, respectively compounds of poly (vinyl chloride) / poly (vinylidene chloride) for the food industry was unnoticed of intermediate levels of radiation [12].

An article by a group of Chinese researchers [14] show how the citric acid can cross-link starch and improve the tensile strength, thermal stability and decrease the dissolution of starch films in water and formic acid. The poor mechanical properties and water stability of starch have restricted its industrial applications. Although cross-linking is a common approach to improve the properties of starch products, current starch cross-linking methods are either expensive, toxic or do not impart the desired properties to the cross-linked materials. In this research, the

possibility of cross-linking starch films using citric acid to improve their strength and stability was examined. Citric acid cross-linked starch films show about 150% higher strength than non-cross-linked films and have strength better than most cross-linked starch and synthetic polymer blended films previously developed. Films cross-linked with 5% citric acid had only 35% loss in weight after being in formic acid for 5 h at 50^0C whereas the non-cross-linked films dissolved immediately [14].

2. Experimental

This first study refers to the study of thermal stability of citrus esters synthesized with feature of plasticizers [15], used to obtain the polymers used then as food packaging.

This type of citric esters [16] was obtained by the reaction of citric acid with 2 - (p-nonyl-phenoxy) ethanol and an aliphatic alcohol with 8, 10 and 13 carbon atoms in the molecule and structures defined by the following general formula:

$$CH_2-COO-R_2$$
$$HO-C-COO-R$$
$$CH_2-COO-R_1$$
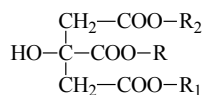
where: $R_2 = $ -CH$_2$-CH$_2$-O-C$_6$H$_4$-p-R$_3$;

$R_3 = $ -C$_9$H$_{19}$;

R_1 and R can be the same and it represents a radical derived from aliphatic alcohols of type 2-ethyl hexyl, isodecil şi isotridecil, or can be different and radical R_1 is of 2-ethyl hexyl, isodecil and isotridecil type and R represents a radical R_2, respectively the limit situation where R and R_1 are identical to R_2 resulting an symmetrical triester.

In order to simplify this, the synthesized products were coded as follows:

C n.m

where: - C - comes from citric acid;

- n - the number of carbon atoms in the aliphatic alcohol; when there are branched alcohols, n is preceded by the prefix *iso*

- m - the number of 2 - (p-nonyl-phenoxy) ethanol molecules added.

This forms two series of compounds:
• Series 1, consisting of compounds C 2-6.1, C iso 10.1 and C iso 13.1;
• Series 2, composed of compounds C 2-6.2, C iso 10.2 and C iso 13.2 (richer in aromatic content);
• and a symmetric triester C 0.3.

Based on this classification can follow changes all the properties depending on the considered structure. Thus, within each series can be seen property development depending on the length of aliphatic alcohol. By comparing terms in the two series counterparts can be seen aromatic content influence function on the basic criteria considered and on the physico-chemical characteristics.

The thermogravimetric analysis was used to determine the thermal stability of the synthesized citric esters.

The TG analysis was performed with a NETZSCH model TG 209. Approximately a 7 mg sample was heated in an Al$_2$O$_3$ crucible with 5^0C/ min under nitrogen gas conditions and with a temperature range from 20 to 900°C.

3. Results and Discussion

Table 1 presents the spectral characteristics and Table 2 presents the principal physico-chemical indices of these products.

Data analysis allows observing the following:
- IR spectras reveal the validity and variability of proposed structures;
- density shows a gradual and smooth change in both series;
- refractive index variation highlights the effect of aromatic content. Within each series the values are very close, almost identical (difference appeared only in the fourth decimal place);
- analytical values of saponification index are close to the theoretical, highlighting the validity of the proposed structures;
- dynamic viscosity depends on the ester structure analysed. In a series, dynamic viscosity increases with increasing length of aliphatic alcohol used in the synthesis. Also, the viscosity terms of the series 2, those that have a high content of aliphatic-aromatic radical is superior to the terms of the series 1. Observed the very high viscosity for citric triesters symmetric (C 0.3). All components have a pseudoplastic character.

In Tables 3 and 4 are listed the results of these measurements, the maximum of the decomposition rate (^{0}C), respectively the temperature at which the total mass loss occurs, compared with DOF (primary plasticizer-standard), respectively the DOS (secondary plasticizer-standard)

In Figure 1, are shown the comparative TG thermograms of compounds C 2-6.1 and C 2-6.2, and in Figure 2, the corresponding compounds of C iso 10.1 and C iso 10.2. In Figure 3, is shown the weight loss for the C 0.3. In Figure 4 is shown the weight loss for the DOF (primary plasticizer-standard) and in Figure 5 is shown the weight loss for the DOS (secondary plasticizer-standard).

In Figure 1 and Figure 2, respectively in Table 3, it is observed that series 2 compounds, richer in aromatic component (C 2-6.2, C iso 10.2, C iso 13.2), have better thermal stability than those of series 1.

According to Figure 3 and Table 3 the symmetrical citric triesters (C 0.3) is the most stable (total weight loss at 633^0C).

In Table 3 and Table 4, respectively in Figure 4 and Figure 5 is shown that all analyzed plasticisers, has a high thermal stability in comparison with standards (DOF and DOS).

In Table 4 it is observed that in the series 2, the temperature at which mass loss is 100%, decreases with

increasing length of the aliphatic alcohol use (up to 531^0C for C 2-6.2), while the effect is reversed in series 1 (up to 437^0C for C iso 13.1).

Good thermal behavior was observed, for all the compounds synthesized, up to 200^0C, level by which weight loss is most likely is due to evaporation rather than decomposition. At $330\text{-}340^0$C, all compounds undergo decomposition, decay.

TABLE 1. Spectral caracteristics

Product	Spectral data
C 2-6.1	IR ν $_{max}$ (cm^{-1}): 3502m ($ν_{OH}$), 2959i ($ν^{as}_{CH3\ alif.}$), 2873i ($ν^{s}_{CH3\ arom.}$), 1740i ($ν_{C=O,\ esteri\ saturați}$), 1511 ($ν_{sch.\ arom.\ +\ δCH(i)}$), 1461i, 1186i, 829i (benzen di- 1,4-) ^{1}H-RMN (CDCl$_3$, 200MHz): 0,87 (m), 1,20 (m), 1,56 (m), 2,87 (m), 4,00 (m), 4,12 (m), 4,69 (s), 6,82 (d), 7,18 (m) ^{13}C-RMN (CDCl$_3$, 50MHz): 8,63; 11,06; 14,04; 22,97; 23,34; 28,67; 30,12; 38,67; 43,29; 61,3-73,15; 113,90; 155,98; 156,27; 169,57; 169,95; 170,17; 172,41; 173,47
C 2-6.2	IR ν $_{max}$ (cm^{-1}): 3508m ($ν_{OH}$), 2960i ($ν^{as}_{CH3\ alif.}$), 2930i, 2873i ($ν^{s}_{CH3\ arom.}$), 1739i ($ν_{C=O,\ esteri\ saturați}$), 1511 ($ν_{sch.\ arom.\ +\ δCH(i)}$), 1247i, 1186i, 739i
C izo 10.1	IR ν $_{max}$ (cm^{-1}): 3503m ($ν_{OH}$), 2958i ($ν^{as}_{CH3\ alif.}$), 2930i, 2872i ($ν^{s}_{CH3\ arom.}$), 1741i ($ν_{C=O,\ esteri\ saturați}$), 1511 ($ν_{sch.\ arom.\ +\ δCH(i)}$), 1248i, 1186i, 739m
C izo 10.2	IR ν $_{max}$ (cm^{-1}): 3502m ($ν_{OH}$), 2958i ($ν^{as}_{CH3\ alif.}$), 2929i, 2872i ($ν^{s}_{CH3\ arom.}$), 1741i ($ν_{C=O,\ esteri\ saturați}$), 1511 ($ν_{sch.\ arom.\ +\ δCH(i)}$), 1248i, 1186i, 828m
C izo 13.1	IR ν $_{max}$ (cm^{-1}): 3504m ($ν_{OH}$), 2958i ($ν^{as}_{CH3\ alif.}$), 2927i, 2872i ($ν^{s}_{CH3\ arom.}$), 1741i ($ν_{C=O,\ esteri\ saturați}$), 1461 ($ν_{sch.\ arom.\ +\ δCH(i)}$), 1248i, 1186i, 828m
C izo 13.2	IR ν $_{max}$ (cm^{-1}): 3503m ($ν_{OH}$), 2958i ($ν^{as}_{CH3\ alif.}$), 2928i, 2872i ($ν^{s}_{CH3\ arom.}$), 1741i ($ν_{C=O,\ esteri\ saturați}$), 1511i, 1248i, 1186i, 829m

TABLE 2. Values of the main physical and chemical parameters [15]

Product	Molecular formula	Density, d_{20}^{20}, g/cm^3	Refractive index, n_D^{20}	Saponification index, mg KOH/g		Dynamic viscosity[a], cP, 20^0C
				teor.	analit.	
C 2-6.1	$C_{39}H_{66}O_8$	1.0096	1.4835	254,27	250,15	1151-1258
C 2-6.2	$C_{48}H_{76}O_9$	1.0290	1.4985	211,46	209,08	6362-7940
C iso 10.1	$C_{43}H_{74}O_8$	0.9929	1.4832	234,44	232,12	1544-1587
C iso 10.2	$C_{50}H_{80}O_9$	1.0120	1.4983	204,28	202,57	8408-8754
C iso 13.1	$C_{49}H_{86}O_8$	0.9744	1.4830	209,88	208,68	1653-1809
C iso 13.2	$C_{53}H_{86}O_9$	1.0029	1.4980	194,37	193,30	8408-8754
C 0.3	$C_{57}H_{86}O_{10}$	1.0450	1.5180	181,00	180,66	184000-270600

^{a} Pseudoplastic behaviour

TABLE 3. The weight loss for the synthesized products

Temp., ^{0}C	C 2-6.1	C 2-6.2	C iso 10.1	C iso 10.2	C iso 13.1	C iso 13.2	C 0.3	DOF	DOS
20-200	1,57	1,02	1,90	0,83	0,78	0,73	0,72	19.22	11.55
250	6.90	6.20	7.68	6.77	5.72	6.74	6.21	34.77	27.41
300	22.12	17.63	20.07	15.99	14.59	15.09	15.60	100	98.30
350	69.28	52.59	68.27	45.96	53.67	46.69	50.67	100	99.96
400	100	95.42	99.21	94.38	97.95	96.62	94.61	100	100
450	100	99.45	100	99.56	100	100	97.93	100	100
500	100	99.79	100	99.90	100	100	98.62	100	100
550	100	100	100	100	100	100	99.18	100	100
600	100	100	100	100	100	100	99.68	100	100
650	100	100	100	100	100	100	100	100	100

(Weight loss, % — left axis label)

TABLE 4. Data from TG termograms for the synthesized products

Product	Maximum of the decomposition rate (^{0}C)	Total weight loss (^{0}C)
C 2-6.1	347.8	398
C 2-6.2	357.7	531
C iso 10.1	346.6	433
C iso 10.2	362.1	521
C iso 13.1	351.9	437
C iso 13.2	361.0	432
C 0.3	353.3	633
DOF	279.5	296
DOS	289.5	362
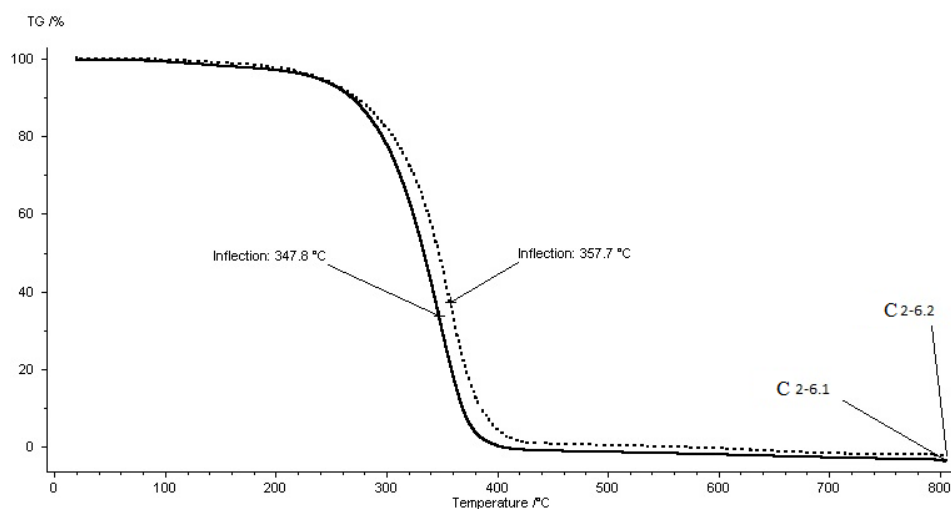
Figure 1. TG termograms for C 2-6.1, C 2-6.2
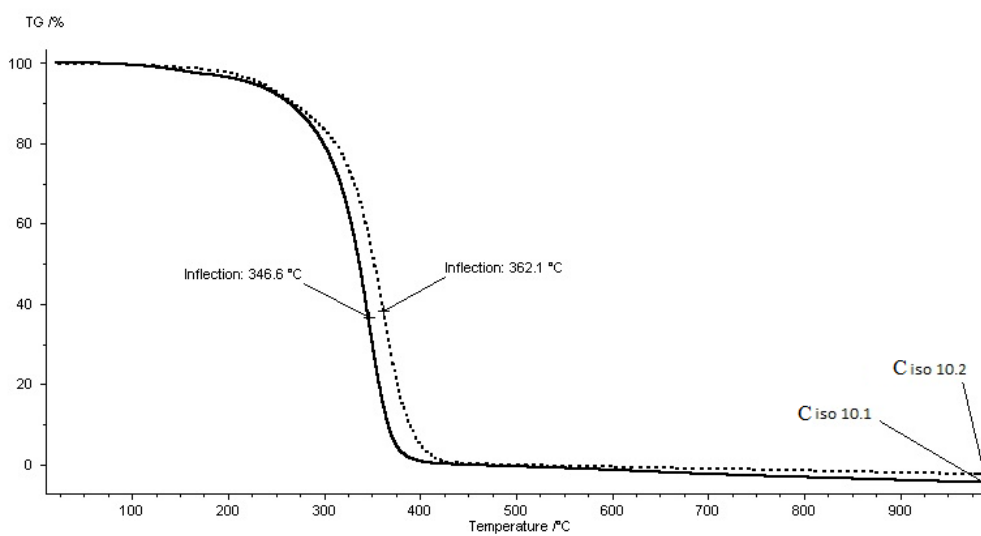
Figure 2. TG termograms for C iso 10.1, C iso 10.2
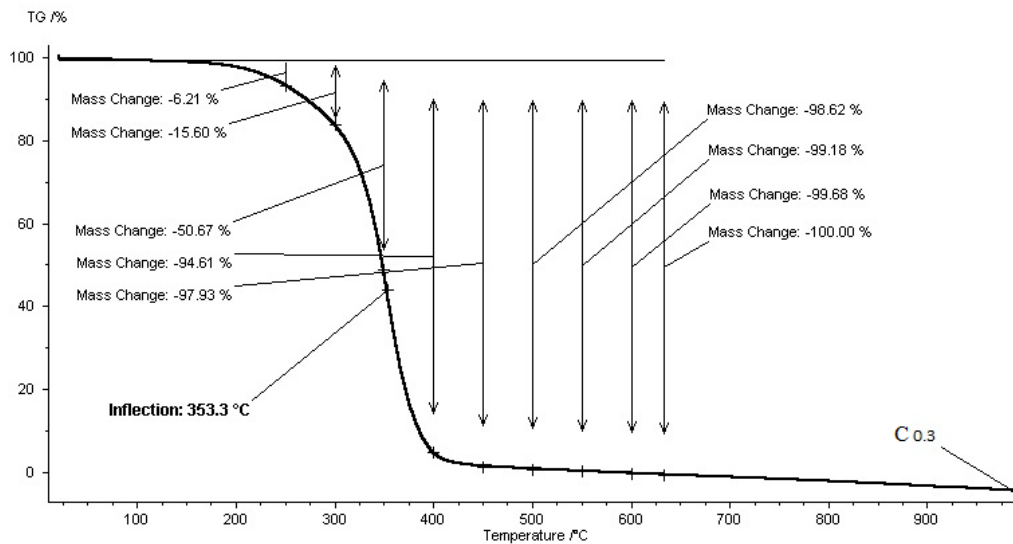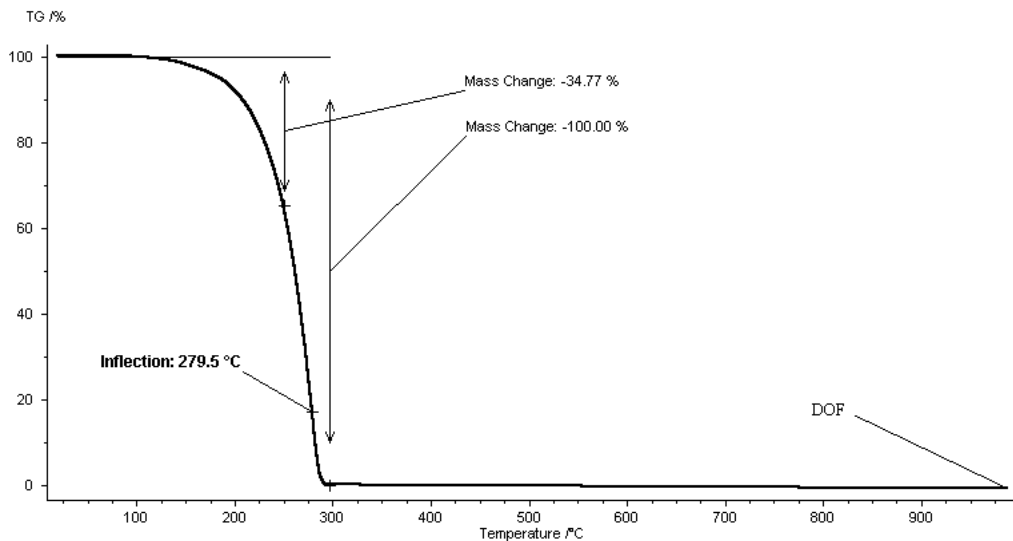
Figure 3. TG termograms for C 0.3
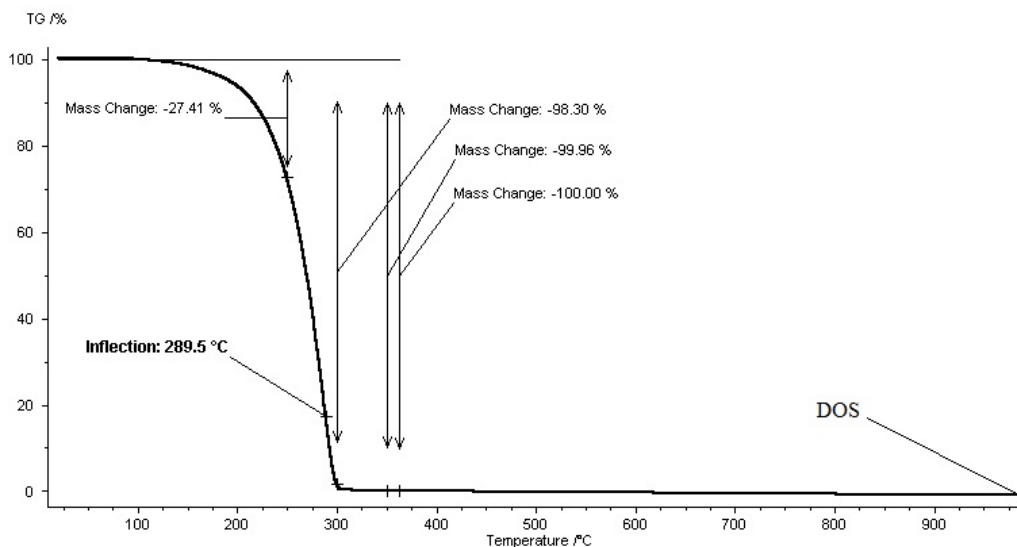

Figure 4. TG termograms for DOF

Figure 5. TG termograms for DOS

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4. Conclusions

Based on all the above stated, it is concluded that these citric esters have a high thermal resistance, even better than the DOF's (primary plasticizer-standard), respectively the DOS's (secondary plasticizer-standard), being able to predict a specific use in areas where these features are required.

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