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CITRUS BUTANOL ESTERS HAVING PLASTICIZING AND LUBRICANT CHARACTERISTICS OBTAINED IN A BUBBLE COLUMN TYPE REACTOR

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ABSTRACT. The aim of this paper was the synthesis of some citric esters with potential biodegradable properties and their use as plasticizers or PVC lubricants. Citric esters were obtained in a bubbling column-type esterification reactor, using citric acid as the acid component, and monoethylene glycol, n-butanol, t-butanol as the hydroxyl components. The esters were characterized by FT-IR spectrometry to reveal the existence of the esteric bonds. Esters present a good thermal stability. The TCS criterion shows a level of compatibility specific to secondary plasticizers. There is a similarity between the values of the tested compounds and the standard DOF regarding hardness. The breaking strength are better and the values of elongation at break are close to the considered standards. The esters prove a very good migration towards rubber and are comparable to tribological fluids. The four balls test showed that without additives and at a test level of 40 daN for 60 min time period, the diameters of the wear spot are generally very good, being in the range of 0.43-0.62 mm. By adding oils, their behavior improves. The welding load values are also good (200-220 daN). The synthesized citrus esters have clear characteristics of plasticizers and/or lubricants for PVC.

Keywords: *citrus esters, bubble column reactor, plasticizer, lubricant*

INTRODUCTION

Currently, special emphasis is placed on the low-energy technologies where the synthesis of environmentally friendly products that have plasticizer and/or lubricant properties are obtained.

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Esters represent a particular importance both in the field of auxiliaries for polymer processing (plasticizer or lubricants) as well as in the field of fluids with applications in tribology.

Citric acid (2-hydroxypropane-1,2,3-tricarboxylic acid) is a weak tribasic organic acid. In nature it is found in citrus fruits and in the human and animal body as metabolic intermediate in citric acid cycle. The uses of citric acid as an acidifier, flavoring, chelating agent [1] and active ingredient in some commercial cleaning products have led to the industrial production of about two tons per year. Citric acid esters have technical applications in the field of lubricants, hydraulic fluids or transformer oils [2].

Citrus esters with potential biodegradable properties, synthesized by classical esterification methods, have clear characteristics of plasticizer and lubricant, respectively [3-6].

Column reactors with bubbling are used at present in many chemical processes [7-10] because they may intensify the heat exchange and may diminish the energy consumption [11-16].

The industrial development leads to an increase in pollution, thus environmental protection represents an important and actual concern [17-20]. In this context, energy efficiency is the most cost-effective way of cutting carbon dioxide emissions and improvements environmental quality [21].

The present paper presents the obtaining of some citrus esters in a low energy consuming bubble column reactor. The products were tested as possible lubricants and plasticizer, revealing that they have adequate or even superior properties to traditional ones.

REZULTS AND DISCUSSION

Physical-chemical properties of the synthesized citrus esters are presented in Table 1, where P1 – citric ester with monoethylene glicol and *n*-butanol and P2 - citric ester with monoethylene glicol and *t*-butanol.

Table 1. Physical-chemical properties of the synthesized citrus esters

Property	P1	P2
Aspect	viscous	viscous, transparent
Color	yellow	colorless
Acid index, mg KOH g^{-1}	< 1	< 1
Refractive index, (20°C)	1.2546	1.2247
Density (25°C), g cm^{-3}	1.2275	1.2311

It may be noticed that although the both esters are viscous, as expected, the other physical-chemical properties are slightly different. P1 is yellow (a very light color) and P2 is colorless, the refractive index of P1 is greater with 2.4%, while its density is smaller only with 0.3% than of the P2. Acid index is below 1 for the both citrus esters.

FT-IR spectra reveal the presence of citrus esters. As an example the FT-IR spectrum for the P1 is presented in Figure 1. The compound structure was confirmed by the presence of the main characteristic bands: 2979 cm^{-1} $(\nu_{CH_3}^{as})$, 1165 cm^{-1} (ν_{COC}^{as}), 1324 cm^{-1} (ν_{COC}^{as}), 1720,3 cm^{-1} $(\nu_{C=O}^{as}\ in\ ester)$.

TG/DTG, DSC/DDSC analysis were also performed and presented in Figure 2 for P1, as an example. The TG curve reveal a continuous mass loss in the studied temperature range. The steps are difficult to separate on the TG curve but the decomposition steps can be distinguished by analyzing the DSC and DDSC curves. One is at 294.4^{o}C and the other over 600^{o}C. The major mass loss at the inflection point is 45.29%, and the maximum occurs before 500^{o}C. After the characterization of the obtained citrus esters as organic compounds, they were investigated as plasticizers and lubricants for PVC.

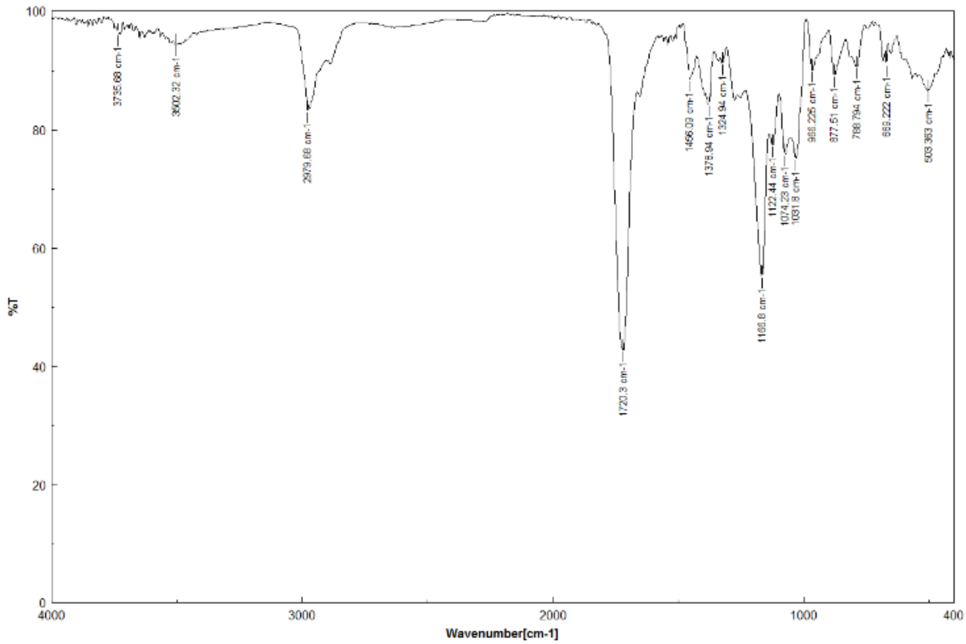

Figure 1. FT-IR spectrum for the citrus ester P1

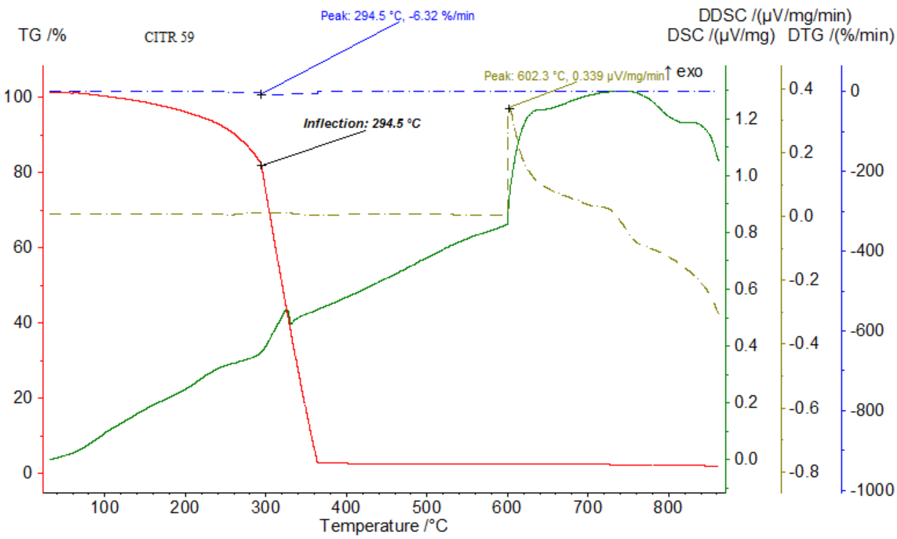

Figure 2. TG/DTG, DSC/DDSC curves obtained for citrus ester P1

Plasticizer investigations. In order to analyze the plasticizer properties, tests were performed that define the compatibility, namely the TCS criterion. Results are presented in Table 2. For comparison meaning, four classic DOF, DOA, DOS and DBF plasticizers were tested under the same conditions.

Table 2. Compatibility tests value of the TCS criterion

Test	P1	P2	DOS	DOF	DOA	DBF
TCS, ^{0}C	148-150	149-150	157-158	117	142	89

There is a level of compatibility specific to secondary plasticizers.

In order to appreciate the products efficiency, Shore A hardness and traction test (100% modulus, elongation at break and breaking strength) were performed, results being presented in Table 3.

In terms of hardness there is a similarity between the values of the tested compounds and the values entered for DOF (standard, a classic representative of the class of primary plasticizers).

The 100% module has values much higher than the value corresponding to the DOF, which indicates a relatively low level of efficiency from this point of view. Very good values of breaking strength are found, compared to the considered standards (DOF and DOA), while the values of elongation at break are close to those of DOA and DOF.

Table 3. Test efficiency for the citrus esters

Tests		P1	P2	DOF	DOA
Shore A Hardness, ^{0}Sh	3"	82.6	89.6	85.0	68.6
	10"	81.7	89.0	84.0	65.3
Traction tests	100 % Modulus, kgf cm^{-2}	182	247	88	112
	Elongation at break, %	249	253	324	333
	Breaking strength, σ_r, kgf cm^{-2}	340	426	156	192

Tests for permanence, which define the plasticizers anchoring capacity in the polymer matrix were also performed, results being presented in Table 4.

Table 4. Test for permanence for the citrus esters

Proprieties		P1	P2	DOF	DOA
Migration towards rubber, 24h / 70^{0}C, %, -		2.25	3.7	4.86	3.21
Water rezistance, 24h / 20^{0}C	Absorbtion, %, +	0.42	0.36	0.19	1.55
	Extraction, %, -	0.55	0.12	0.17	3.42

The migration towards rubber values are slightly smaller than the DOF, but comparable to DOA. The water resistance is placed at the same level as DOF. All the products tested in this respect prove a very good migration towards rubber, the values obtained being between the necessary ones and the standards. The resistance to extraction with water and oil is also very good. Thus, from this point of view we can say that the analyzed compounds have the characteristics of a primary plasticizer.

Concluding it may be affirmed that the citrus esters present plasticizer properties, especially as a secondary plasticizer used in polymer processing.

Physical constants and rheology. Analyzing some of the physical properties and of the rheology of the obtained products reveal that they are comparable to tribological fluids, that is high flammability points and the flow points values and kinematic viscosity that have similar variation (Table 5).

Table 5. Values of the main physical constants and rheology of the citrus esters

Citrus esters	Kinematic viscosity, mm^2/s		Flammability points, ^{0}C	Flow points, ^{0}C
	40 ^{0}C	100 ^{0}C		
P1	200.0	17.4	261	-18
P2	187.3	12.6	261	-20

Lubricant investigations. In order to determine the lubricant capacity of the obtained citrus esters, the four balls test was performed, results being presented in Table 6.

Table 6. Ware stain diameter and four ball test for the citrus esters

Citrus esters	Without additives	With aditive of 1.5% Zn dithiophosphat		With aditive of 1.5% Zn dithiocarbonate	
	Ware stain diameter, mm,	Ware stain diameter, mm	Welding, daN	Ware stain diameter, mm	Welding, daN
	40 daN, 60 min	40 daN 60 min		40 daN 60 min	
P1	0.48	0.48	200	0.46	200
P2	0.71	0.62	260	0.65	240

The results show that in the case of species without additives and at a test level of 40 daN for 60 min time period, the diameters of the wear spot are generally very good, placing in the range of 0.43-0.62 mm. Adding oils in all cases leads to a slight improvement in behavior. The welding load values are also good and a level of 200-220 daN is constantly reached. The results for the compounds with additives show a good compatibility of these synthetic oils with anti-wear additives.

CONCLUSIONS

The aim of this paper was the synthesis of some esters based on citric acid and their evaluation in order to be used as plasticizers and as lubricants for PVC. Citric esters were obtained in a bubbling column-type esterification reactor, using citric acid as the acidic component and monoethylene glycol as the hydroxyl component in conjunction with *n*-butanol, *t*-butanol.

Due to the intrinsic biodegradability characteristics brought by the citrus skeleton, it is accepted that the synthesized citrus esters have the ability not to negatively influence the environment. The obtained esters were characterized by FT-IR spectrometry in order to reveal the existence of the esteric bonds - 1720,3 cm^{-1} ($\nu^{as}_{C=O}\ in\ ester$). The TG/DTG, DSC/DDSC analysis was used to determine their thermal stability and degradability, revealing a remarkable thermal stability. The TCS criterion presents a level of compatibility specific to secondary plasticizers. There is a similarity between the values of the tested compounds and the standard DOF in terms of hardness. The 100% module indicates a relatively low level of efficiency from this point of view. The breaking strength are better and the values of elongation at break are close to the considered standards (DOF and DOA). The esters also prove a very good migration towards rubber and that they are comparable to tribological fluids, because of their high flammability points and the flow points values and kinematic viscosity that have similar variation. The lubricant capacity of the obtained citrus esters was performed using the four balls test, revealing that without additives and at a test level of 40 daN for 60 min time period, the diameters of the wear spot are generally in the range of 0.43-0.62 mm. By adding oils, their behavior improves. The welding load values are also good and a level of 200-220 daN being constantly reached. The obtained results certify that the synthesized citrus esters have clear characteristics of plasticizers and/or lubricants for PVC, in particular as secondary plasticizers used in the polymers processing.

EXPERIMENTAL SECTION

Ester synthesis. The synthesis takes place in two stages. First, the citric acid, the monoetylene glicol, the other hydroxyl components (in the proportions 1:2:1) and the catalyst (*p*-toluenesulphonic acid) – 0.1%, are introduced into a flask equipped with a water-cooled rising refrigerant and a thermometer, where a pre-esterification reaction takes place under continuous stirring in a preheating nest (Figure 3).

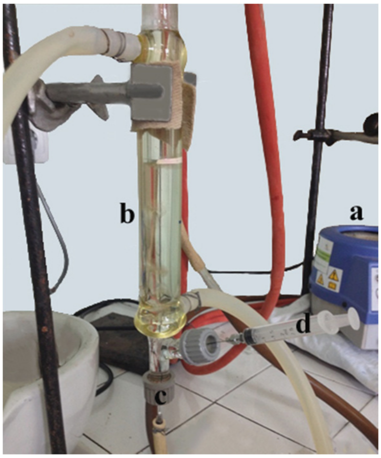

Figure 3. Ester synthesis experimental installation
(a) preheating nest; **(b)** bubble column reactor; **(c)** bubbling nozzle; **(d)** sampling

After one hour, the reaction mass is cooled to 80°C, and the resulting product is transferred directly into the esterification column reactor with bubbling (Figure 3), which was preheated to 80°C. The synthesis takes place at reflux temperature, without removing the reaction water from the system. The esterification reaction is monitored by periodically determining the acid index throughout the synthesis.

Analyzing methods. *Physical-chemical properties*: Aspect – visual; Refractive index – Abbe refractometer; Density, at 20°C – pycnometer; Acid number - according to SR ISO 3682.

FT-IR spectra were recorded with a Bruker Vertex 70 spectrometer (Bruker Daltonik GmbH, Germany) equipped with a Platinium ATR spectrometer, Bruker Diamond type A225/Q.I.

Thermogravimetric analysis (TG)/(DTG) and differential scanning calorimetry (DSC) were performed with NETZSCH STA apparatus STA449F1A 449F1-0220-M. A quantity of between 3 ÷ 7 mg sample was heated in a crucible of Al2O3, with the rate of 5⁰C/min., under a nitrogen atmosphere in the temperature range of 25 ÷ 900⁰C.

Evaluation of P1 and P2 synthesized esters as plasticizer: TCS criterion was determined with the Boetius microscope, using a PVC suspension Kw = 67. In order to evaluate the other tests, PCV foils were realized, which were roundly or squarely cut of 5 cm – according to SR EN ISO 2898-2:2003. The Shore A hardness and the traction tests were performed according to SR EN ISO 846:2000. For the water resistance investigation, the square foil was immersed in distilled water at 20±2°C for 24 hours. The volatiles were determined at 100±2°C for 24 hours. The plasticizer migration was determined with the round foils at 70±2°C for 24 hours using rubber absorbent discs. Oil stability was determined at 20±2⁰C for 168 hours.

Evaluation of P1 and P2 synthesized esters as lubricants. Flammability point was determined according to ASTM D 92, in a tank of 50 mm in diameter, buried in the sand, over which the flame is passed. Flow disorder point was determined according to ASTM D 97. The kinematic viscosity and the viscosity index were determined using the Ubbelohde viscometer, according to ASTM 445.

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