

## Application of “Green chemistry” principles to the modification of carbohydrates from natural sources for bio-additives in plastics

D. Vassilev<sup>1\*</sup>, N. Petkova<sup>2</sup>, D. Yaneva<sup>1</sup>, P. Denev<sup>2</sup>

<sup>1</sup>Technical University of Gabrovo, Department of Mathematic, Informatic and Natural Sciences, 4, H. Dimitar Str., 5300 Gabrovo, Bulgaria

<sup>2</sup>University of Food Technologies, Department of Organic Chemistry and Inorganic Chemistry, 26 Maritsa Blvd., 4002 Plovdiv, Bulgaria

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Interest in sucrose esters which are surfactants and environmental products, attracts the attention of researchers and manufacturers, due to the fact that renewable, easily available raw materials are used for their production. Sucrose esters are non-toxic, biocompatible and biodegradable products that are widely used in food technology, cosmetics and medicine. Many industrial technologies generate waste that poses a risk of environmental pollution. The research activity in recent years is aimed at the search for new technological solutions to intensify the processes, by applying the principles of "green chemistry". For reactions taking place in solution, the use of ultrasound is effective. Ultrasound has been found to affect the rate of chemical reactions in solution through the phenomenon of cavitation. In the synthesis and modification of organic compounds, research related to the application of ultrasound in the preparation of esters is promising, as is the aim of the present work - reduction of reaction time, increase of yields, use of safe raw materials, reduction of energy consumption. The intensifying effect of ultrasound effect in the transesterification of methylcaprate with sucrose, catalyst  $K_2CO_3$  at room temperature was demonstrated, sucrose caprate being obtained with a significant minimization of reaction time. The characterization of the obtained ester was carried out by FT-IR,  $^1H$  and  $^{13}C$  spectroscopy. The potential plasticizing effect of the synthesized ester was evaluated. Polyvinyl chloride was used, with different amounts of the synthesized ester added. PVC polymer films with different ester concentrations were prepared and analyzed by differential scanning calorimetry and mechanical tests (modulus of elasticity).

With the use of ultrasound energy during the process, a reduction in reaction time, use of safe raw materials, and a reduction in energy consumption were achieved. From the data obtained on the glass transition temperature and mechanical tests, we can expect an application of the ester as a biodegradable additive with plasticizing properties.

**Keywords:** green chemistry, sucrose ester, bio-plasticizer, bio-additives

### INTRODUCTION

Polyvinyl chloride (PVC) is one of the polymers with extensive application. PVC has specific properties attributed to the chlorine atoms in its molecule. Its advantages are high strength, corrosion resistance and accessibility, and this leads to widespread application both in building materials, domestic and industrial products. However, the fragility of PVC limits its use [1-8].

Plasticizers are important additives in the industrial production of plastics, including PVC. Plasticizers contribute to uniform mixing and compatibility by effectively weakening the intramolecular bonds of polymer chains. This improves the plasticity of the material, making it more flexible and plastic while improving the characteristics of the product. Different types of plasticizers are available, with phthalate plasticizers being widely used [9-12].

Plasticizers are major additives in the processing of polyvinyl chloride (PVC), phthalates being exten-

sively utilized. However, they have been proven harmful to human health and the environment, necessitating the use of bio-alternatives.

Phthalate plasticizers, including dioctyl phthalate, dibutyl phthalate, di-(2-ethylhexyl phthalate) and diisononyl phthalate, are the most common plasticizers in PVC processing [13, 14]. Dioctyl phthalate (DOP) has excellent compatibility with PVC due to its low molecular weight, allowing it to be easily inserted between polymer molecules and providing high plasticization efficiency, and it is very popular for modifying PVC materials [15, 16]. However, the application of DOP in the food and pharmaceutical industry is limited by the hazard to human health and the environment [17]. Therefore, there is a growing need for the development and study of new plasticizers that are non-toxic and environmentally safe. Of the esters of aliphatic acids, the most commonly used as plasticizers are stearates and oleates, especially for compositions with plasticity at low temperatures. This group also includes sebacinates and adipinates, but their

\* To whom all correspondence should be sent:  
E-mail: [dvasilev@tugab.bg](mailto:dvasilev@tugab.bg)

production is limited by their high cost and high volatility [4-6].

The present study uses the bio-resource sucrose to obtain suitable alternatives to conventional plasticizers, using ultrasonic synthesis to obtain an ester of sucrose with the higher fatty acid – capric acid.

## EXPERIMENTAL

For the synthesis, an ultrasonic bath DimoffA-2/2, with generator power of 100W, and frequency of 44 kHz was used. Chimtex® AR reagents were used – sucrose, capric acid, sodium sulfate anhydrous (Na<sub>2</sub>SO<sub>4</sub>), sodium, methanol, hexane.

### *Thin-layer chromatography (TLC) for monitoring the progress of the reaction*

Thin-layer chromatography was performed on silica gel Kieselgel 60 F254 plates (Merck, Germany). Two variants of elution were used with different mobile phases.

Variant A: The TLC plate was developed in three different types of mobile phases as follows: 1. Chloroform: methanol: water 85/13.5/1.5 v/v/v; 2. Chloroform/methanol/acetic acid 98.5/1.5/1.4 v/v/v and 3. n-hexane/diethyl ether/acetic acid 70/30/1 v/v/v.

Variant B: The TLC plate was developed in a mobile phase consisting of ethyl acetate/methanol/water 17:2:1 v/v/v. TLC spots were visualized by spraying with 10% sulfuric acid in methanol and heating at 120°C for 5 min.

### *FTIR spectroscopy*

FTIR spectra were recorded on a Nicolet Avatar spectrometer (Thermo Scientific, USA, ZnSe crystal) on KBr pellets in the frequency range from 4000 to 500 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup> and 132 scans. The absorption was reported in wavenumbers (cm<sup>-1</sup>).

### *<sup>1</sup>H and <sup>13</sup>C NMR spectroscopy.*

The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker spectrometer (500 MHz frequency) in CDCl<sub>3</sub> with tetramethylsilane (TMS) as a standard. The chemical shifts (δ) were expressed in ppm.

### *Synthesis of methyl caprate*

In a round-bottom flask with a ground glass joint, the appropriate 0.0035 moles of capric acid were weighed out. Then, 250 ml of hexane and 1 dm<sup>3</sup> of 1% H<sub>2</sub>SO<sub>4</sub> in CH<sub>3</sub>OH were added. The flask was connected to a water-cooled reflux condenser and heated in a water bath at a temperature of 68-70°C. After 120 min the reaction was interrupted, and the reaction mixture was cooled to room temperature.

100 ml of distilled water was added and neutralized with 10% Na<sub>2</sub>CO<sub>3</sub>. The sample was extracted three times with hexane. The collected extracts were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was distilled to yield methyl caprate.

### *Synthesis of sucrose caprate*

In an Erlenmeyer flask, 50 ml of methanol was placed and appropriate amounts of methyl caprate, sucrose, and the catalyst sodium methylate were weighed in their respective molar ratios (1:1). The mixture was sonicated at 40°C. After the reaction stopped, the synthesis was stopped, and the solvent was distilled. The residue was dissolved in 25% NaCl / n-butanol 1:1 and partitioned with a separatory funnel. After separation of the phases, the organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Then, the solvent was distilled, and the resulting sucrose caprate was obtained.

### *Investigation of the applicability of the obtained ester as a bio-plasticizer*

For the purposes of the experiment, commercial polyvinyl chloride (PVC) without colorants, stabilizers, and fillers (EMKA®), was used. As a bio-plasticizer of polyvinyl chloride, the ultrasound-synthesized sucrose caprate was used at a concentration of 10, 20, 30, 40%. The experimental studies were carried out with samples in the form of polymer films prepared by casting from a solution in tetrahydrofuran using the following methodology: the amount of polyvinyl chloride weighed on an analytical scale was placed in a beaker and 100 cm<sup>3</sup> of tetrahydrofuran was added to it. The mixture was heated in a water bath at 40°C until the polyvinyl chloride was completely dissolved, then the weighed amount of sucrose caprate was added. The resulting solution was homogenized for 2 h, then poured into a Petri dish and left at room temperature until the solvent had completely evaporated. The film was dried at room temperature in a vacuum dryer [3].

The thermal properties of the resulting films were investigated by differential scanning calorimetry (DSC). The measurements were carried out on a scanning calorimeter DSC 204 F1 Phoenix (NETZSCH Gerätebau GmbH) in argon medium, with a heating flow rate of 20 cm<sup>3</sup>/min at the following temperature modes:

- Heating from 20°C to 200 °C at a speed of 10 K/min (first scan);
- Isothermal mode at 200 °C for 3 min;
- Cooling in liquid nitrogen from 200 °C to –50 °C, with a cooling rate of 10 K/min;
- Isothermal mode at -50 °C for 5 min;

- Heating from -50 °C to 200 °C at a speed of 10 K/min (second scan).

The weight of a single sample of each specimen was 2.5-4.2 g. The glass transition temperature  $T_g$  was determined on the second scan as the inflection point of the thermogram. The processing was carried out with specialized software PROTEUS for DSC 204 F1.

Strength indicators were determined with *Lloyd LSI* tensiometer, in uniaxial tensile deformation at a speed of 100 mm/min at room temperature, on samples with a width of 10 mm. Using the specialized dynamometer software, the values of the breaking voltage (MPa) and the modulus of elasticity (MPa) were calculated for each sample. For each content of sucrose caprate, 9-12 samples were examined, and the results were averaged.

## RESULTS AND DISCUSSION

In the IR spectra, several areas characteristic of carbohydrates stand out - about 3300  $\text{cm}^{-1}$  there is a wide asymmetrical band due to the valence oscillations of -OH. The strong interaction between the structural elements of the macromolecules in the modified sucrose is the reason in the spectrum considered, bands arise due to complex vibrations, which can be defined as oscillations of both the furanose ring and the macromolecule as a whole. Stretching vibrations (C-C), (C-O), (C-O-C) of the furanose structure are observed between 1000 and 1200  $\text{cm}^{-1}$ . Depending on the degree of substitution, the maximum of this band is shifted and at the same time the half-width changes. This is due to the hydroxyl groups that form the hydrogen bonds, as well as to the esterification of some of them.

In the  $^1\text{H}$  NMR spectrum of sucrose caprate, two regions can be distinguished - in the range 0-3 ppm characteristic of methyl and methylene protons from the acid and 3.0-5.0 ppm characteristic of protons from the carbohydrate part, which are shown in Table 1. The chemical shift for methyl group protons in sucrose caprate is observed at 0.96~0.99 ppm. The signals for protons from the methylene groups are in the range of 1.31~2.36 ppm. Glucose protons of glucopyranose are observed in the range of 3.39~5.40 ppm and glucose protons of fructofuranose - 3.62~4.52 ppm.

In the  $^{13}\text{C}$  NMR spectrum, signals that are typical of the carbonyl carbon atom at 174.36 ppm are observed. Signals for methyl carbon atoms are observed in the range of 14.02 ppm. The signals of the carbon atoms of the pyranose, respectively, of the furanose ring, are observed in the range 62.26-108.18 ppm, with carbon atoms from the pyranose ring being at the lower frequencies and for the

furanose at the higher frequency range. In order to investigate the applicability of sucrose caprate as bio-plasticizer for PVC, the data from the DSC analysis of the tested samples (Table 2) were analyzed.

**Table 1.** Chemical shift ( $\delta$ , ppm) in the  $^1\text{H}$  NMR spectrum

Group	Chemical shift ( $\delta$ , ppm) for sucrose caprate
$\text{CH}_3-$	0.96~0.99
$-(\text{CH}_2)_n-$	1.31~1.68
$-(\text{CH}_2)_n-\text{CH}_2-\text{O}$	2,34~2,36
$-\text{O}-\text{C}-\text{H}-\text{O}$	5.39~5.40
H-Glc	3.39~5.40
H-Fru	3.62~4.52

**Table 2.** Dependence of the glass transition temperature  $T_g$  on the ester content of the sample.

Content of sucrose caprate in PVC, %	Glass transition temperature $T_g$ , °C
0	80.5
10	59.3
20	60.9
30	62.8
40	64.6

The results obtained from the thermograms show the presence of only one inflection point (one glass transition temperature) in the thermograms of the studied films, which points to the good mixability between the esters and PVC. The glass transition temperatures of the test specimens depending on the content of the esters are presented in Table 2. There is a significant decrease in  $T_g$  with increasing ester content, which is a confirmation of its plasticizing effect on PVC. When the content of the esters increases, there is a sharp decrease in the glass transition temperature. For a more detailed study of the mechanical and strength characteristics and the change of the elastic properties, tensile deformation tests were conducted, calculating the parameters: stress at break, Young's modulus, elongation at break.

The results (Table 3) show that as the content of sucrose caprate increases, the modulus of elasticity decreases and the elongation at break of the sample increases. The change in tensile strength (breaking tension) of the sample depending on the sucrose caprate content indicates that the tensile strength decreases. Data from DSC and mechanical tests show a plasticizing effect of sucrose caprate in the polyvinylchloride film as it reduces the glass transition temperature, the modulus of elasticity and the breaking tension and increases the relative elongation at break.

**Table 3.** Mechanical properties of PVC containing sucrose caprate.

Ester content, %	Stress at break, MPa	Young's Modulus, MPa	Elongation at break, %
0%	52.4	1483.0	5.5
10%	24.5	746.3	80.5
20%	17.8	634.8	99.6
30%	16.9	540.6	124.3
40%	15.8	506.3	143.8

### CONCLUSION

In response to the requirements for plasticized PVC in terms of environmental friendliness and health considerations, traditional plasticizers can be replaced with bio-based and environmentally friendly plasticizers derived from renewable resources, thus expanding the scope of application of PVC and its products.

The tested applicability of ultrasound-derived sucrose caprate as a bio-additive with a plasticizing effect in polyvinyl chloride was confirmed by differential scanning calorimetry, determining the effect of the ester on the glass transition temperature  $T_g$ . It was found out that the increase of its quantity results in decrease of polymer  $T_g$ , i.e. the flexibility of macromolecules increases, which is a prerequisite for higher deformability. This supports the conclusion that the ester mixture has a plasticizing effect. This is also confirmed by the mechanical properties of the PVC films used with different ester contents.

The results obtained at this stage of the study allow to conclude that sucrose caprate can be applied as a bio-additive with a plasticizing effect in polyvinyl chloride.

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