

Examination of essential oils used in PLA with GC-MS method

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Abstract— *Upto date, many experiments have been carried out successfully in producing and using essential oil-treated biodegradable polylactid acid (PLA), but the examinations revealed. That essential oils, theoretically consisting the same composition, (like cinnamonoil, majoram oil, orclaryoil) crystallize differently in the PLA base, weakening its mechanical, optical, and thermal properties. The aim of the experiment is to define the exact components with a Gas-Chromatography instrument with MS-detector. It has been found that among the compounds detected in different cinnamon oil samples, there are indeed other potentially harmful components, such as serpentines, alcoholic derivatives, mineral oils and phthalic acid esters, which have caused the condition to deteriorate.*

Keywords— *biopolymer, essential oils, GC-MS, phthalic acid esters, PLA.*

I. INTRODUCTION

One of the major environmental problems of the 21st century is non-degradable polymers, which are manufactured in huge amounts all over the world because their cheap prices and their easy use make our lives easier. In Hungary, the amount of usable plastic waste is increasing every year. Nowadays, the primary aim of our polymer research is to produce polymers that meet the requirements of this age, that are biodegradable, and compatible with the tissues of the human body.

In one of our former research we compared the mechanical, optical, and thermal properties of samples containing different antimicrobial additives, a base material, and a polyoleicacid type suitable for foil making. It was necessary for the additives to not weaken the material's above-mentioned properties. The research revealed that essential oils, theoretically consisting of the same composition (like cinnamon-oil, majoram-oil, orclary-oil) crystallize differently in the PLA base, making differences in its mechanical, optical, and thermal properties.

II. MATERIALS

2.1 Polyacticacid (PLA)

Biopolymers can be sorted based on their raw materials and the method of production. There are three different types of biopolymers: polysaccharide- based (starch, cellulose), protein-based (collagen, gelatin, casein, keratin), and polymers with vegetal origin (wheat gluten, maize casein, soy protein). These function as raw materials for long-used natural based plastics.

An important group of biopolymers are the polymers made by monomers produced by fermentation. These include polylactides such as polylactic acid and poly-hydroxy-alcanoates. Polyester amide, polyester urethane, polyglycolic acid and polylactides are biodegradable synthetic polymers, but we can also find degradable polymers consisting of organic or synthetic components such as the starch/PVAL, or starch/PLA coupling. The polylactic acid, as the material that meets the above-mentioned requirements has been at the center of researches for decades, and the analysis of its reactions in the literature is really important. PLA is a biodegradable, thermoplastic polymer, which can be produced from renewable raw materials. Due to its properties, it has proven to be suitable to make deep-drawing products (for example glasses, or fruit boxes) and can also be used in packaging technologies. The production of lactic acid (LA) based on crops has revolutionized the production of PLA, thus opening the way for the production of custom plastics and packaging materials. Nowadays, this technology represents 80% of the used methods. The quantitative distribution of PLA produced in the world is shown in Figure 1:

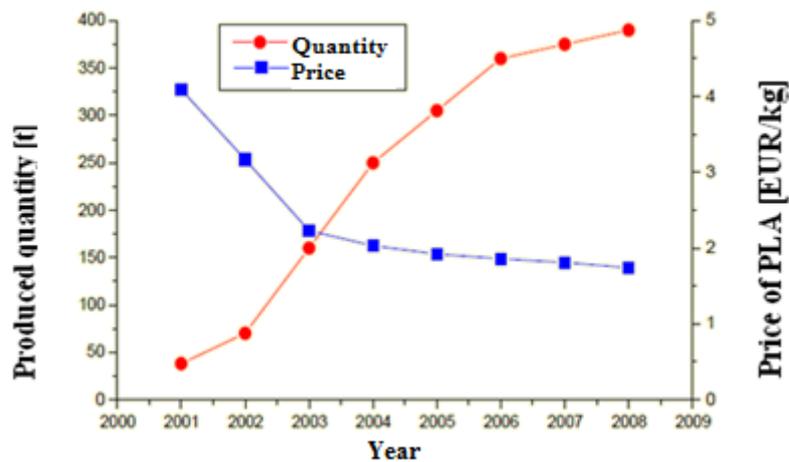


FIGURE 1. The relationship between the quantity (EUR / kg) of PLA produced from 2000 up to 2009. [1]

Lactic acid (also known as 2-hydroxypropanoic acid, C₃H₆O₃) is an organic acid that play a role in many biochemical processes (Scheele, 1780.) The molecule consists of a carboxyl group and a hydroxyl group, this way creating an alpha hydroxy-acid (AHA). A proton from a carboxyl group leads to solution, and the resulting ion is called lactate. It is hygroscopic, and highly miscible with water or ethanol. A chiral molecule having an asymmetric carbon atom has two distinct spatial isomers (Figure 2). One of them is L - (+) - lactic acid, while its mirror image is called D (-) - lactic acid. Only the L - (+) - lactic acid is significant biologically, typically a product of anaerobic metabolisms. By hydrogenating the pyruvic acid, the following isomers may be formed:

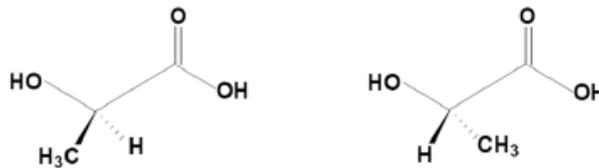


FIGURE 2. Two isomers of lactic acid: D - (-) lactic acid and L - (+) lactic acid [2]

D-lactic acid occurs in natural yeast and sour cabbage, while L-lactic acid can be found in beef and lump milk. Two lactic acid molecules form a cyclic compound in water, which is the dimer of lactic acid: lactide, which exists in three spatial forms due to an asymmetric carbon atom in lactic acid [3]:

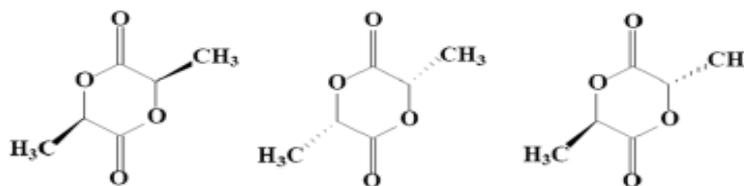


FIGURE 2. Dimers of lactic acid [3]:

A. L-lactide B. D-lactide and C. Meso-lactide

The structure and properties of PLA. PLA belongs to the group of polylactides which is a linear aliphatic polyester. The repeating unit is lactic acid (Figure 3.), its physical properties are influenced by many factors: structure, molecular characteristics, crystallinity, morphology and chain orientation. Physical, chemical and biological properties determine its usability.

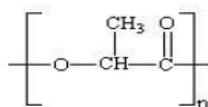


FIGURE 3. Lactic acid, the monomer of PLA [3]

The physical properties of PLA are improving if the material is orientated, in case of making a fiber, a two-way film or a deep drawn product. Today, a monomer mixture is used, which consists mostly of a mixture of L, and D-lactic acid in ~ 0.1 to 10 % content. The mechanical properties, the crystallinity, the degradability of the PLA can be adjusted within the ratio of L- and D-lactic acid (higher crystallinity PLA decreases slower). If PLA contains less than 8 % D-lactic acid, it partially crystallizes by frothing, tempering or stretching. Strength and heat resistance increase with crystallinity. When the D-isomer ratio decreases in the chain, the melting point of the PLA increases and could reach 170-190 ° C. PLA's surface tension is 38 N/m, therefore the printing or metal coating of the material is relatively simple. Of course, in the case of a particular structure, the conditions of manufacturing also significantly influence the properties of the polymers.

2.2 Essential oils

Essential oils extracted from plants, there have antibacterial effects and each other has other beneficial (medicinal) effects depending on their composition. There is also a difference between the microbial effect of essential oils, many examples of which are found in the literature [4, 5, 6, 7, 8]. Essential oils can consist of more than 50 ingredients, including up to 85 % of the main components, while some minor components can only be traced. Essential oils are mainly composed of terpenes and terpenoids (oxygen-containing terpenes): monoterpenes (C10) or sesquiterpenes (C15) but in smaller amounts diterpenes (C20) and triterpenes can also be found (Figure 4.). In addition to the terpenes, other major constituents may be the various low molecular weight aliphatic and aromatic compounds, e.g. hydrocarbons, acids, alcohols, aldehydes, lactones and sulfur-containing volatile compounds. The amount and proportion of components may vary depending on weather, geographical distribution, and individual variation within plants (Burt, 2004) [6, 7, 8].

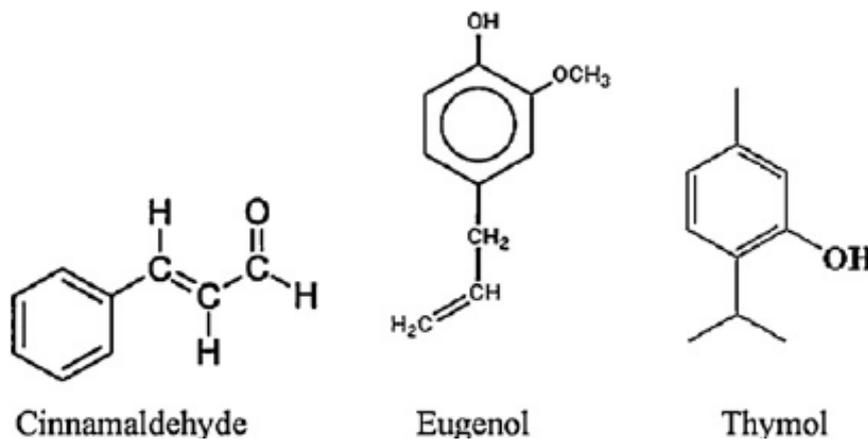


FIGURE 4. The structure of some essential oil components [9]

In the essential oils approx. 90% monoterpenes are found as the main ingredient. Monoterpenes are formed by the condensation of two isoprene molecules and can be classified into several groups based on their diverse functional groups: hydrocarbons, which may also be cyclically structured (terpines, pinenes, sabin); alcohols (linalool, geraniol); aldehydes (geranium, neral); ketones (carved, camphor); esters (linalyl acetate), phenols (thymol, carvacrol). Components containing aromatic rings, such as cinnamaldehyde, cinnamon alcohol, eugenol, estragol, etc., are less common (Bakkali et al., 2008).

2.3 Chemical composition of controlled oil samples

A. Cinnamon oil (*Aetheroleum cinnamomi*)

Obtained by distillation of water or steam through Ceylon cinnamon tree belonging to the Lauraceae family (Lauraceae) (*Cinnamomum verum*, syn.: *C. ceylanicum*) inner bark and Chinese cassia cinnamon (*C. aromaticum*, syn. : *C. cassia*) Unpurified bark where the yield of the oil is around 0.5 to 4.0%. In addition to the bark, the cinnamon leaf leaves and leafy shoots also produce essential oils, the main components of cinnamon aldehyde and eugenol, the total amount of compounds for bark oils: 65-75% or 5-18%, and 3-5% in leaf (cinnamon aldehyde) or 70-90% (eugenol).

B. Majoram oil (*Aetheroleum majoranae*)

Majoranna oil is extracted from the dry shoots of majoranna (*Origanum majorana*) by steam distillation. Pale yellow, yellowish or amber, strongly spicy and penetrating. Component: terpinen-4-ol (38.4%), cis-szabinene hydrate (15.0%), p-cymol (7.0%) and γ -terpinene (6.9%) [10].

C. Musk oil (*Salvia sclarea*)

It is obtained from the musk oxide by steam distillation. In addition to the cosmetics industry, it is also used in the food industry and in medicine because it has an antiseptic effect. Component: Linalil-acetate and linalool make up nearly 80%, approx. 10% sclararene and a much smaller amount of camphor, mircene, geraniol, caryophylline, germacle, terpinol, peacock, pineapple and borneol. [11]

D. Ginger oil (*Aetheroleumzingiberis*)

Obtained from the root gum by steam distillation. It is a spicy, sweet, slightly lemon, with a spicy aroma. Its color is yellow, pale. Component: Sesquiterpenes: α - and β -zingiberen (30-40%), turmeric (18%), bizabenol (10-15%) [11].

III. GC-MS ANALYSIS METHOD

The purpose of the chromatographic procedures is to ensure the qualitative and quantitative determination of the volatile organic matter content of the samples. Separation is based on the re-distribution of components between two phases, and chromatographic procedures differ from other distribution-based separation methods (eg liquid-liquid extraction, distillation) so that one of the phases involved in separation is in motion (mobile phase), the other phase is stationary (stationary phase). The chromatogram is generated by the eluting components of the column to represent the intensity of the signal induced in the detector by the time.

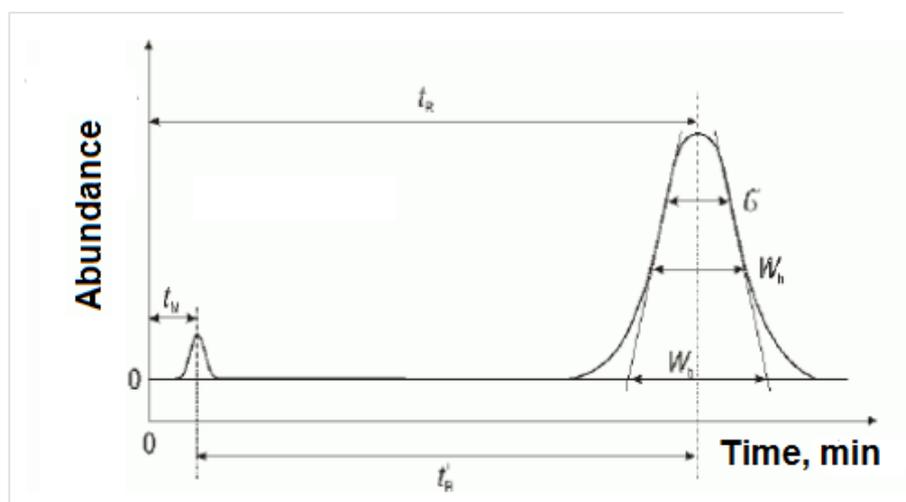


FIGURE 5. An ideal chromatogram

3.1 Description of gas chromatography processes

Retention time (R_t) of a given component is the time from injection to detection (peak maximum). All components spend the same time in the carrier gas. Components that do not interact with the stationary phase simply pass through the carrier gas on the column, their passage time is the dead time (t_m) determined by the column length and the flow rate of the carrier gas which is dependent on the temperature of the column. The partition coefficient (K):

$$K = \frac{C(\text{stationary})}{C(\text{carrier})} \quad (1)$$

Where:

- K : the partition ratio of a given component,
- $C_{\text{stationary phase}}$: equilibrium concentration of a given component in the stationary phase,
- C_{carrier} : equilibrium concentration of a given component in the carrier gas.

The partition coefficient characterizes the affinity of each component to the stationary phase at a given temperature. The higher the K value for a given component the longer the time is spent in the stationary phase, the greater its retention time. So, injected at once 59 components reach the end of the column in different times, so separation can occur. While the time

spent in the carrier gas can be characterized by dead time, the time spent in the stationary phase is given by the corrected retention time (tR'):

$$tR' = tR - T_m \quad (2)$$

In the chromatogram the quality information provided by retention times and the volume is carried by the areas under the peaks. To determine the quality of each component, the retention data is sufficient only if the sample profile of the sample is known (in our case it contains explosive substances but no interfering components). If we do not have such information, the identification of the components can be done only by using suitable detectors (eg MS) [12].

IV. RESULTS

The relationship between the concentration of the samples and the analytical signal (peak area) is determined by calibration. The area of the peaks of the chromatogram shows a linear relationship with the amount of material in the detector generally, increasing the amount of material to saturation. For quantitative analysis, usually the straight section of the curve (dynamic range of the detector) can be applied. Since the sensitivity of the detectors (the slope of the calibration line) is different for each material, the calibration should be performed for each component to be determined. As expected, there were significant differences in the composition of cinnamon oil samples, which can be seen in Figures 6 and 7:

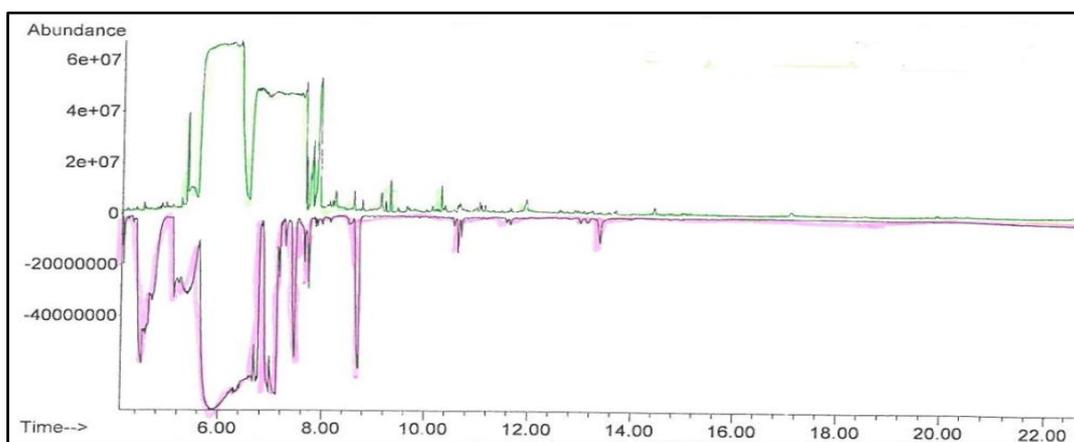


FIGURE 6. Comparative chromatogram of cinnamon oil samples

It can be stated that the chromatograms differ significantly of sample 1 of cinnamon oil (green line) and cinnamon oil sample 2 from the 7th minute, which means that their chemical composition is different. After the qualitative determination, the components detected in the samples were compared for given retention times. Alignment until $t = 5.81$ min retention time was observed, indicating the presence of cinnamaldehyde in all four samples. It can be said that the main component is present in the system. There are now significant differences in the chromatogram, for example at $t = 6.94$ minutes in the cinnamon oil sample 2, 2-propen-1-ol and at $t = 8.50$ min. benzyl benzoate was detected, while in cinnamon oil sample 1 none of them was detected at all. It can be assumed that they are components that can cause the crystallization difference.

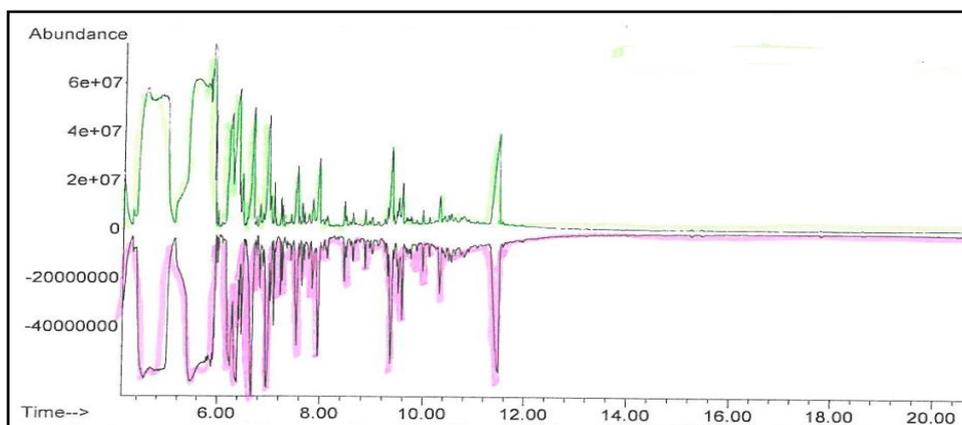


FIGURE 7. Additional chromatograms of cinnamon oil samples

V. SUMMARY

The GC-MS chromatographic analysis of the PLA biopolymer containing different essential oils showed that there was a significant difference between the composition of the cinnamon oil samples and not between the muscatel sage and the ginger oil samples. The measurement results were not influenced by the sample preparation method, since the essential oils were naturally solved so that the decomposition could be more easily made in the system and it was easier to detect the components that formed the oils. In addition to the components already disclosed, the following compound, such as benzyl benzoate (*Figure 8*), which is used as a solvent for perfume for tobacco, as well as for improving the plasticity of polymers and cellulose, has been detected.

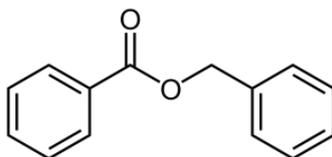


FIGURE 8. Structural Formula for Benzylbenzoate [13]

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