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VEGETABLE OILS: POSSIBLE NEW PLASTICIZERS IN THE RUBBER INDUSTRY

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Abstract: The main goal of the research was to answer the question whether vegetable oils can be used as natural plasticizers for the rubber industry. To find out, we analyzed four types of vegetable oils (olive, rapeseed, sunflower and castor oil) by thermal analytical methods (DMA, TSDC) and compared the results with each other. Two hypotheses were set up, one is that vegetable oils will behave as a kind of macromolecule. The other hypothesis was that different fatty acid composition results in different relaxation processes and glass transition temperatures. Both of the hypotheses proved to be correct.

Keywords: vegetable oils, oil, plasticizers, thermal analytical method, DMA, TSDC

INTRODUCTION

The advantages of using vegetable oils in the plastics industry are as follows: they are renewable materials, their low price, and their environmental impact is moderate [1]. Using vegetable oils as plasticizers is not an over-researched area, there are only few studies about this topic, but oils could be important new materials, because they reduce material costs, without significant deterioration of the properties. Furthermore, there is a negative image in the consumers mind about phthalic acid esters, hence new plasticizers of natural origin could get better judgement.

1. MATERIALS AND METHODS

1.1. Materials

Oils are built of triglycerides, which consist of fatty acids and glycerin linked to each other. Fatty acids are carboxylic acids, they can be divided into two groups, depending on whether they contain a double bond, or not: saturated (do not contain double bond) and unsaturated (contain double bond) fatty acids. Notation: *Cn: k*, where *n* is the number of carbon atoms, and *k* is the number of double bonds. [2]

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The oil samples' theoretical fatty acid composition was used in the analysis. The composition of the oil samples based on data from technical literature. All mentioned studies determined the composition of the oils by gas chromatography. The data was collected from different studies (olive oil: [3, 4, 5]; rapeseed oil: [3, 5]; sunflower oil: [3, 6]; castor oil: [7], [8, 9]). Then we calculated the theoretical fatty acid values with arithmetic mean. The comparative chart shows only the most important fatty acids *(Figure 1)*. For easier comparability, we labelled the six most abundant fatty acids; the *other* ingredient contains both saturated and unsaturated fatty acids, but they occur in very small amounts in the tested oils.

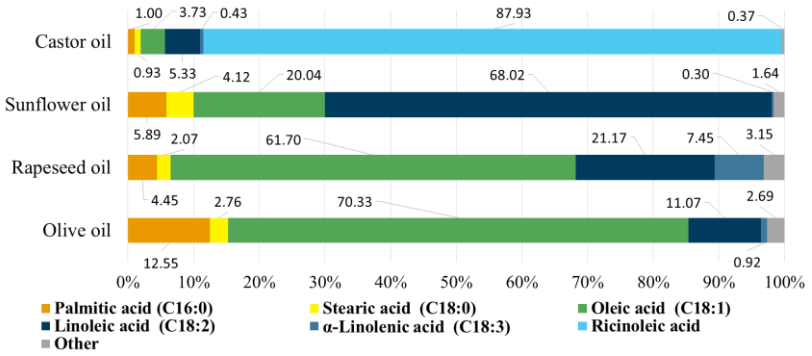

Figure 1
Theoretical fatty acid composition of the oil samples

1.2. Measuring methods

The vegetable oil samples were examined by thermal analytical methods. Thermal analytical methods are suitable for analysing transformation processes. In general, the principle of this type of methods is to measure a property (mass, modulus, etc.) as a function of temperature [10]. The methods can be used on their own, but using several methods at the same time we could get more well-grounded conclusions. In a similar study, Senatra et al. [11, 12] also examined fluids (oil-water emulsion) by thermally stimulated depolarization current, but they compared the results with the results of differential scanning calorimetry.

1.2.1. Parameters of the Dynamic Mechanical Analysis (DMA)

Because of the low viscosity, the shear (rotary) mode would be the only possible way to perform the DMA, thus a new method had to be developed due to the capabilities of the device. Ichemaguba [13] developed a method for testing plasticizers, where he measured 35 × 10 mm rectangular borosilicate glass filter paper impregnated with plasticizer, in dual cantilever mode. We followed this method, however higher capacity 150 g/m^2 non-woven fabric was used in single cantilever mode. This greatly improved the sensitivity of the method. The initial temperature was –120 °C,

and the heating rate was 2 °C/min. Measurements were made at 1 Hz frequency with ± 32 μm deformation.

1.2.2. Parameters of the Thermally Stimulated Depolarization Current (TSDC)

The oils were soaked in borosilicate "glass paper" filter with a pore size of 2.6 μm. According to the preliminary measurements, this material is two orders of magnitude less polarizable than the tested oils. The polarizing temperature was 50 °C, with –120 °C initial temperature. Both the cooling and the heating rate was 5 °C/min. The polarizing electric field strength was 500 V/mm. The evaluation was done with a special program developed by Marossy.

2. RESULTS

2.1. Results of the Dynamic Mechanical Analysis (DMA)

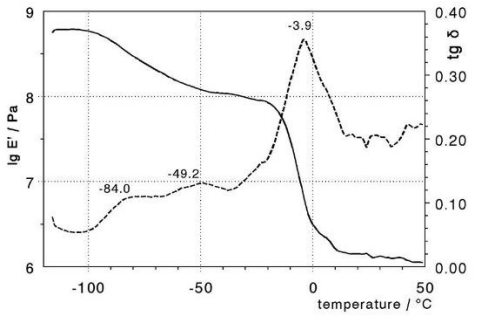

Figure 2
DMA curve of olive oil

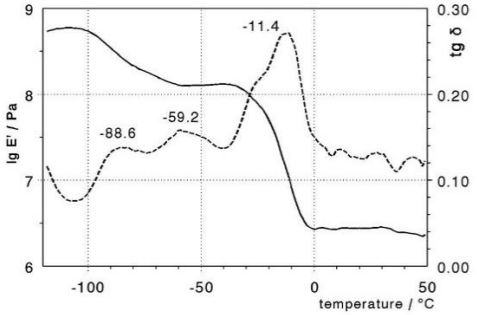

Figure 3
DMA curve of rapeseed oil

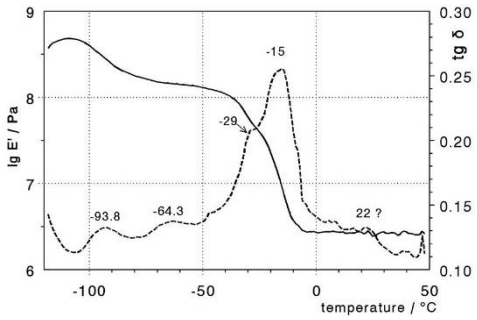

Figure 4
DMA curve of sunflower oil

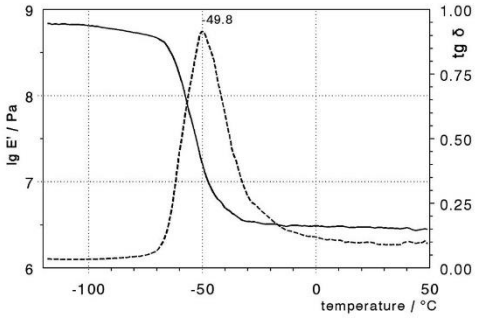

Figure 5
DMA curve of castor oil

The glass transition temperature (T_g) belongs to the highest intensity peak of the mechanical loss factor (tg δ, marked with dashed line), which is the lg E' (storage modulus, marked with a solid line) curve's inflexion point [14].

Olive oil's *(Figure 2)* and rapeseed oil's *(Figure 3)* DMA curves are very similar, they have several transitions, which is indicated by several peaks. According to the theoretical fatty acid composition, these oils have the highest oleic acid content among the four samples, and also have the highest glass transition temperature. From this, it can be deducted that the lower the oleic acid content, the lower the glass transition temperature.

The curve of sunflower oil *(Figure 4)* has the most peaks (four), this indicates four transition processes. Sunflower oil contains the largest amount of linoleic acid. The DMA curve of castor oil *(Figure 5)* is the most similar to the elastomers typical DMA curve. There is only one peak, so only one transition process, and castor oil has the lowest glass transition temperature (–49.8 °C) among the four oils tested according to DMA. This is probably due to the very high content of ricinoleic acid (~90%), which is a special unsaturated omega-9 fatty acid, having a hydroxyl functional group joined its 12nd carbon atom [15]. Thus ricinoleic acid (and castor oil itself) is more polar than most fatty acids. Probably the fatty acids' polarity affects the oils' glass transition temperature: the more polar the oil, the lower the T_g. Furthermore, it can be assumed that ricinoleic acid is a macromolecule, since castor oil shows the characteristic of polymers according to DMA.

Table 1

Glass transition temperatures according to DMA

Oils	Olive oil	Rapeseed oil	Sunflower oil	Castor oil
$\mathbf{T_g}$ [°C]	*–3.9*	*–11.4*	*–15.0*	*–49.8*

Based on the curves, it can also be stated that the olive oil with the largest saturated fatty acid content has the highest glass transition temperature, followed by in descending order – T_g and also in terms of saturated fatty acid content – rapeseed, sunflower and castor oil. It can be concluded that the lower the saturated fatty acid content, the lower the glass transition temperature.

2.2. Results of the Thermally Stimulated Depolarization Current (TSDC)

The alpha relaxation (glass transition) is determined by the main chain's segment movement, whilst the beta relaxation is associated with the side groups' movement [16]. Olive oil's TSDC curve *(Figure 6)* is very similar to DMA: it shows three peaks, so multiple transformations, which suggests that there are independent molecular motions in the material. The peak at –67.5 °C presumably indicates α relaxation, while the other two flatter peaks at –93.5 °C and –39.7 °C indicate β relaxation.

Rapeseed oil' TSDC curve *(Figure 7)* shows only one peak in the –100…–50 °C range (at –87.5 °C), unlike its DMA curve. This peak refers to α relaxation, and this oil has the lowest glass transition temperature according to the TSDC measurements.

Sunflower oil's TSDC *(Figure 8)* and DMA curves are similar. There are four peaks, several transformation processes takes place in it. The three flatter peaks (–107.0, –93.6 and –78.0 °C) may indicate β relaxation, while the peak with the highest intensity (at –23.5 °C) indicates α relaxation.

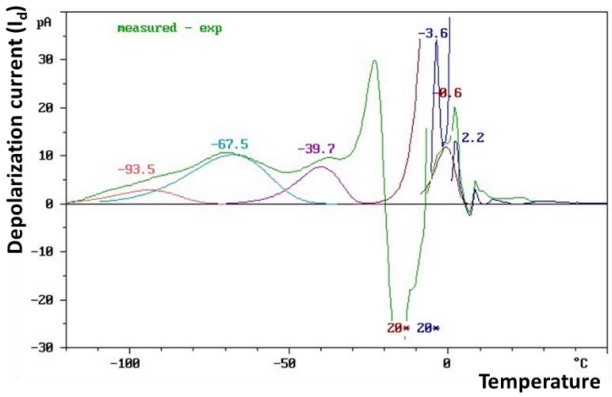

Figure 6
TSDC curve of olive oil

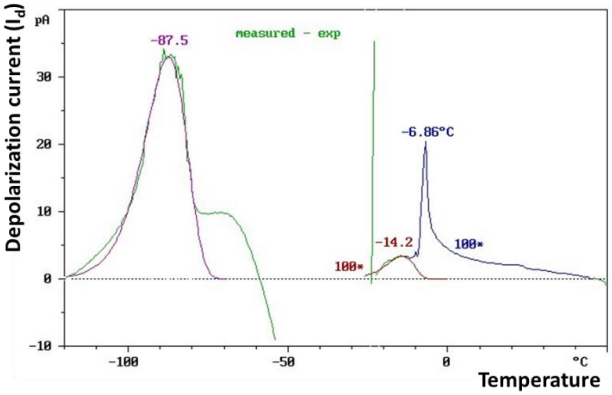

Figure 7
TSDC curve of rapeseed oil

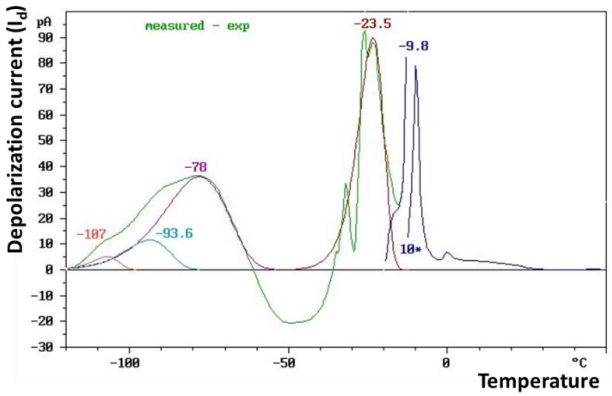

Figure 8
TSDC curve of sunflower oil

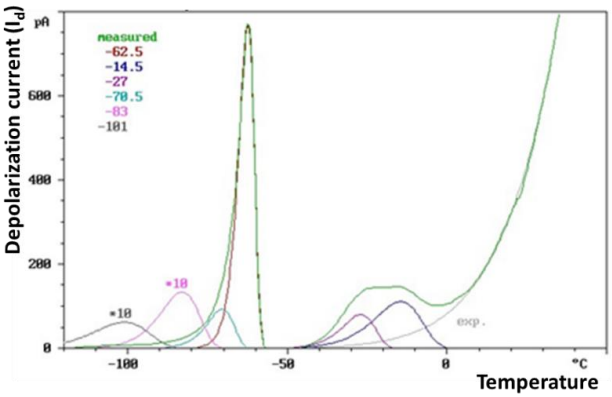

Figure 9
TSDC curve of castor oil

Castor oil's TSDC curve is also similar to its DMA results *(Figure 9)*: one separate, high intensity peak in the –100…–50 °C temperature range, at –62.5 °C, which represents α relaxation. This very high intensity peak (which almost reaches 700 pA depolarization current, much larger than the other oils' largest intensity) is also refers to the castor oil's highly polar nature due to its high content of ricinoleic acid.

Rapeseed oil has the lowest (–87.5 °C), and castor oil has the highest (–62.5 °C) glass transition temperature according to the TSDC measurement.

CONCLUSION

Four different types of vegetable oils (olive, rapeseed, sunflower and castor oil) was tested by dynamic mechanical analysis and thermally stimulated depolarization current. The oils showed similar behavior to macromolecules, thus they can be possible new plasticizers in the rubber industry. Furthermore, different fatty acid composition resulted in different transition processes.

Summarizing the results of DMA and TSDC measurements the following additional findings can be made:

1. We cannot assign a particular glass transition temperature, we can only determine a temperature range.
2. Glass transition temperature also depends on the measurement method.
3. The DMA curve represents the peaks in one block, while TSDC is a more sensitive method with more accurate values, but the sample preparation takes more time in this method.
4. DMA is advantageous if we want faster measurement, and less accurate results are sufficient for us.
5. Based on the DMA curves, I assume that the highest amount of fatty acid in the oils affects the glass transition temperature.
6. As shown in *Figure 10*, there are extreme differences between the identified glass transition temperatures for a given sample (the most outstanding differences are observed for olive and rapeseed oil).

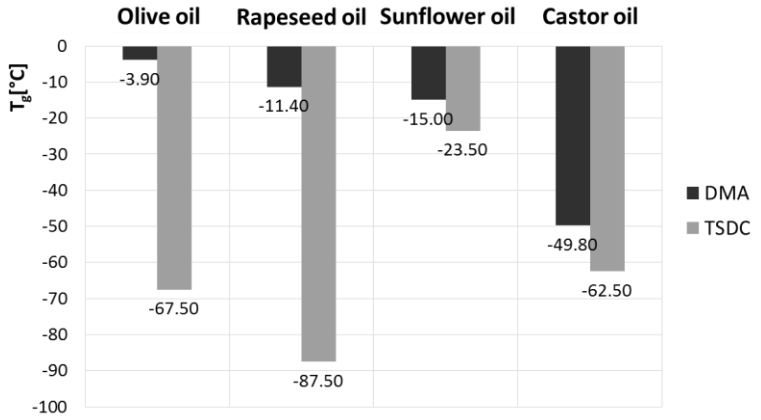

Figure 10
Comparison of DMA and TSDC results

7. In terms of the shape of the curves, castor oil showed the greatest similarity between the two methods, in addition to similar T_g values were also produced. Furthermore, the castor oil's curve shape approaches very well the typical thermomechanical curve of elastomers. This is presumably due to the high lactic acid content (close to 90%), which has a strongly polar character. This sample had the most intense depolarization current peak, approx. seven times larger the other oils'.
8. The curves of olive and sunflower oil also show similarities in both measurement methods, but their shape contains several peaks unlike castor oil. In the case of rapeseed oil, the curves of DMA and TSDC differ significantly in terms of their shape and intensity of peaks.

The transition temperatures can be used to calculate the activation energy, which is the basis of thermodynamic compatibility. The accurate fatty acid composition of the oil samples could be defined by Gas Chromatography-Mass Spectrometry, then the solubility parameter of the natural rubber and the oil plasticizers could be determined. Knowing these data, it is possible to give a theoretical estimation for the rubber mixtures' thermodynamic and chemical compatibility.

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