Biopolymer Foil Materials Examination with DSC and TSD methods

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Abstract— *Thermally Simulated Depolarization Current measurement is an excellent but not widely used method for identifying relaxation processes in polymers. The TSDC method is used here to analyze the molecular movements in biopolymers. Differential Scanning Calorimetry is a technique used to measure thermal properties of polymers based on the rate at which they absorb heat energy compared to a reference material. The two techniques take advantage of the energy changes involved in the various phase transitions of certain polymer molecules. This allows for several properties of the material to be ascertained; melting points, enthalpies of melting, crystallization temperatures, glass transition temperatures and degradation temperatures. The examined biopolymer films are made from biological materials such as proteins and polysaccharides. These materials have gained wide usage in pharmaceutical, medical and food areas. The uses of biopolymer films depend on their structure and mechanical properties. This work is based on three types of alginate, and gelatin films. The films were prepared by casting. The casting technique used aqueous solutions in each case of sample preparation. The manufacturing process of the sodium alginate and gelatin films was a single stage solving process, and for the calcium alginate and alginic acid have a chemical reaction process.*

Keywords— alginate, alginic acid, gelatin, DSC, TSD.

I. INTRODUCTION

The past few years have witnessed rapidly expanding interest in food additives as sources of biomolecules with potential to replace synthetic polymers in medical materials with biocompatibility, bioactivity, biodegradability for unique applications.

Due to biomolecules having become more available, ever increasing demand for high-performance "natural" matrices for biomedical and pharmaceutical applications such as organ regeneration and tissue engineering, gel like bandages, wound dressing, medical suture lines, artifical limbs, controlled drug delivery systems, films, contact lenses and capsules for oral ingestion.[1]

Biopolymer films and biofoils are formed from natural polymers, of animal or plant origin, such as polysaccharides, lipids and proteins. The biopolymers are neutral and always renewable, because they are made from plant materials which can be grown indefinitely.

Alginic acid forms water-soluble salts with monovalent cations, but these are precipitated upon acidification. Alginates of many bivalent cations, particularly of $Ca^{2+,}$ Mg^{2+} are insoluble in water and can be prepared when sodium ions of water soluble Na- alginate are replaced by di- and trivalent cations. The *alginate* extracted from various species of algae (Phaeophyceae), are natural polymers, which have low cost, high stability, good gelling properties, biocompatibility. Thus, these materials have great potential for use in the preparation of biopolymer films, gelling agents, drug coatings for vegetarians (instead of gelatin) or for dental applications. Toxicological data showed that alginates are safe when used in food. The Na-alginate acts as stabilizer and thickener facilitating the dissolution and improving viscosity of the ingredients preventing the formation of crystals that will determine the appearance and homogeneity, mainly in frozen products [1]

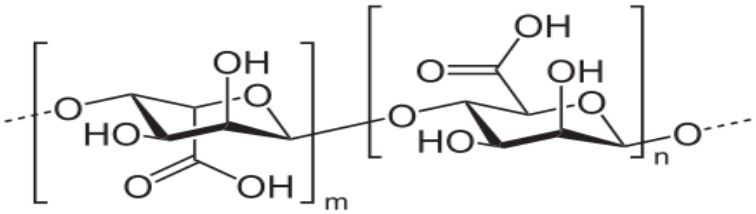

FIG.1. ALGINATE

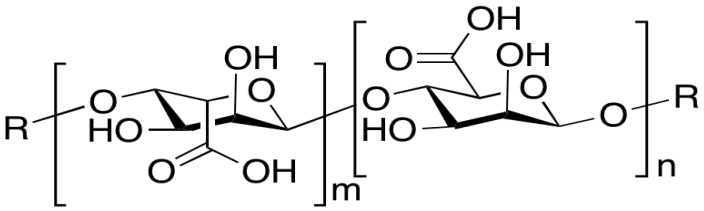

FIG.2. ALGINIC ACID

Gelatin is a mixture of peptides and proteins produced by partial hydrolysis of collagen extracted from the bovine, pork fish or poultry skin, bones, and connective tissues of animals. Gelatin is a typical material used in the medical or pharmaceutical fields [2].

II. EXPERIMENTAL

2.1 Materials

The biopolymer films were produced from sodium alginate (ISP Alginates), calcium alginate, alginic acid, gelatin (food additive). Furthermore, acetic acid, (commercial product) and calcium sulfate (commercial product) were used.

2.2 Prepartion of biofoils

For the used casting techniques the following describes the method for each material. In the case of sodium alginate and gelatin 2 m/m % aqueous solutions were made at room temperature, and drying was carried out in Petri dish at 35°C and 45% humidity. In case the of calcium alginate the sodium alginate alginate solution was sprayed with $CaSO_4$ (2m/m%) solution then the sodium atoms were replaced with calcium atoms. The alginic acid film was prepared from the sodium alginate film. In the first step the dried sodium alginate was soaked in diluted acetic acid. The acidic acid replaces the Na^+ ions to OHgroups. The films were then stored in a desiccator at a relative humidity of 25 %, for a period of three days to reach the equilibrium moisture in this environment before characterization. After sample preparation, molecular movement of the samples was examined with DSC and TSD methods.

2.3 Differential Scanning Calorimetry (DSC)

Dynamic Scanning Calorymetry (abbreviated (DSC) is a technique used to study and characterize materials. The DCS measurements carried out Setaram DSC131 Evo equipment. The heating rate is 10° C/min. The tests started at 20° C and finished at 220 ° C. Before the thermal examinations, the biopolymer samples were held in desiccators to keep the humidity equable.

The DSC thermograms of various alginate film materials shown in Fig. 3. The curves at around 100°C show the water removed from the biofilms however it is depending on the water binding ability of the polymer, this is why it appears at slightly different temperatures in the thermograms. In the case of Na-alginate film the temperature of water emission is at 110°C, and for the Ca-alginate 137°C. The alginic acid's DSC curve is shown in Fig. 4. The thermogram is similar to the Ca-alginate's curve showing two heat absorption areas.

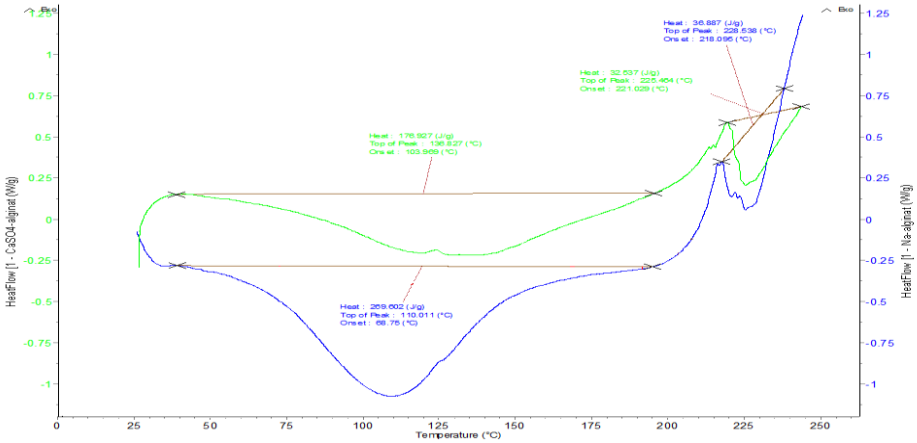

FIG.3. CA-ALGINATE AND NA-ALGINATE THERMOGRAM

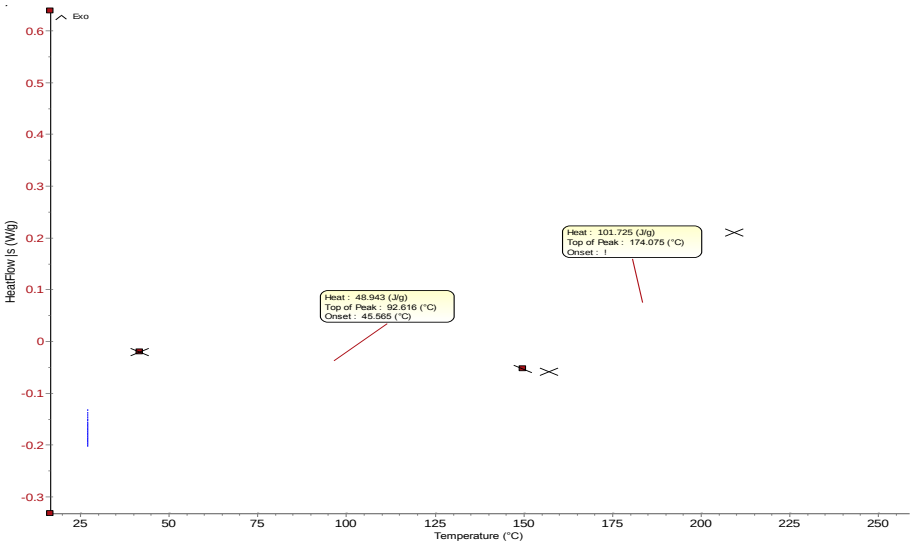

FIG.4. ALGINIC ACID TEHERMOGRAM

In case of the gelatin film the water departure peak is also seen at 130°C.

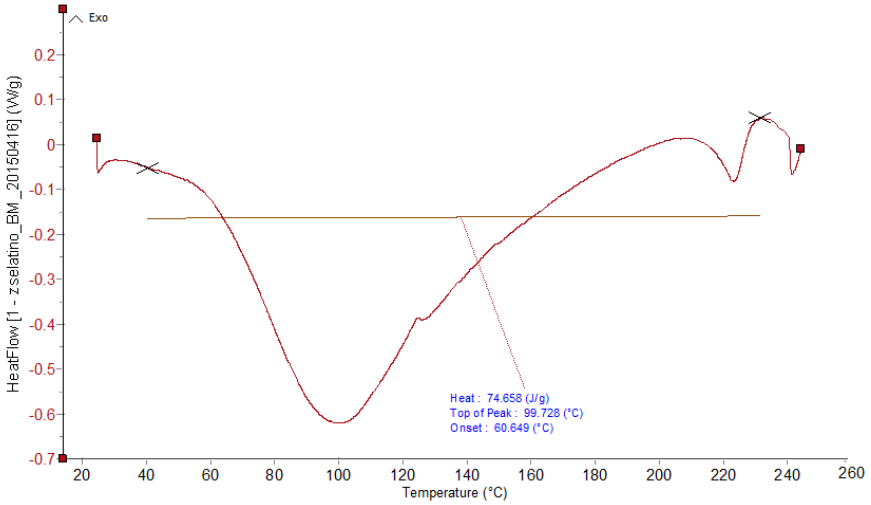

FIG.5. GELATIN THERMOGRAM

2.4 Thermally Simulated Depolarisation Current measurements (TSD)

TSD experiments were carried out on a SETARAM TSC II instrument using helium gas as heat transfer medium. The sensitivity of the instrument is 10^{-15}A.

Gold plated disk samples were used

Polarizing temperature: 125°C

Polarization time: 10 minutes

Polarizing field: 300 V/mm

Cooling : Newtonian

Start temperature: -150°C

Heating rate: 7°C/min (after 10 minutes isothermal at -150°C)

Final temperature: 125°C

Evaluation principle

Although the basic principle of the TSDC is simple, there are two difficulties. The first one is technical, measuring extremely low currents, in case of polar polymers through even 5 decades. The second one is the evaluation and interpretation of the depolarization thermograms. For the analysis of the depolarization processes the method is described in [6], although this paper deals with PVC, i.e. a strongly polar polymer.

Supposing that the relaxation processes follow the Arrhenius law, the relaxation time of dipoles can be calculated as follows

$$\tau_{(T)} = \tau_0 e^{\frac{A}{RT}} \tag{1}$$

where; A is the activation energy of the process.

P_0 polarization is frozen in the polymer during the cooling in electric field. Heating the sample in zero field (short circuited) the decaying polarization at t time is:

$$P_{(t)} = P_0 e^{\left(-\int_0^t \frac{1}{\tau} dt\right)} \tag{2}$$

the liberating charges produce current. The current density is

$$j_{(t)} = -\frac{P_0}{\tau} \exp\left(-\int_0^t \frac{1}{\tau} dt\right) \tag{3}$$

Using a constant b heating rate the temperature of the sample is

$$T = T_0 + bt \tag{4}$$

and the depolarization current density is

$$j_{(T)} = -\frac{P_0}{\tau} \exp\left(-\frac{1}{b}\int_{T_0}^T \frac{1}{\tau} dT\right) \tag{5}$$

Replacing the $\tau(T)$ from eq. (1.)

$$j_{(T)} = -\left(\frac{P_0}{\tau_0}\right) \exp\left[-\frac{A}{RT} - \frac{1}{b\tau_0}\int_{T_0}^T \exp\left(-\frac{A}{RT}\right) dT\right] \tag{6}$$

The equation can be used for $I_{(T)}$ current, too, if the d thickness and A area of the sample is known.

Let $C = AP_0/\tau_0$ and $B = A/Rb\tau_0$, replace $A/RT \equiv s$

$$I_{(s)} = C \exp\left\{-s - B\left[e^{-s}(s^{-2} - 2s^{-3} + 6s^{-4} \ldots\right]_{s_0}^{s}\right\} \tag{7}$$

This equation describes an asymmetric peak as a function of temperature and the A activation energy can be calculated from the half width of the peak as,

$$A = 2.406R\frac{1}{\frac{1}{T_l} - \frac{1}{T_u}} \tag{8}$$

or both from the maximum and lower half

$$A = 1.443R\frac{1}{\frac{1}{T_l} - \frac{1}{T_m}} \tag{9}$$

and the maximum and upper half

$$A = 0.962R\frac{1}{\frac{1}{T_m} - \frac{1}{T_u}} \tag{10}$$

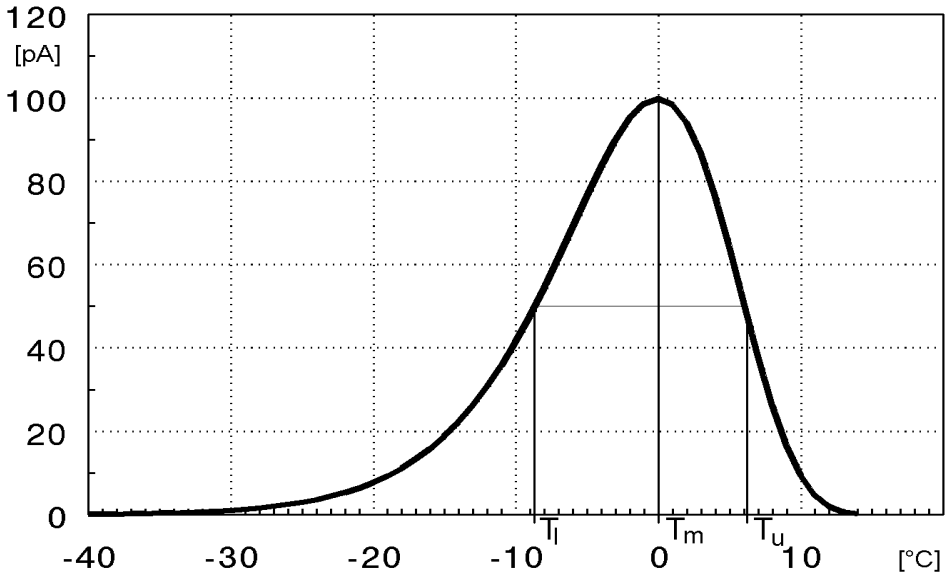

FIG.6. THE SHAPE OF AN IDEAL DEPOLARIZATION PEAK CALCULATED BY EQ. (7.) AND THE TEMPERATURES FOR DETERMINATION OF ACTIVATION ENERGY.

The σ surface charge density can be obtained from the full charge Q and the A area of the sample.

$$\sigma = Q/A \tag{11}$$

The surface charge density can be used for determination of permittivity change of transition Δε; called oscillator strength

$$\Delta\varepsilon = \sigma/E\varepsilon_0 \tag{12}$$

This is the most characteristic to the transition, because does not contain dimensions and electric field.

For evaluation of depolarization current spectra our previously developed software was used. This program calculates the currents for $1kVmm^{-1}$ field and $30cm^2$ electrode area and all current data are picoampers.

In case of zero external field, i.e. in short circuited state the measured depolarization current is the sum of currents of individual processes.

$$I_{d(T)} = \sum_{i=1}^{n} I_{d(T)n} \tag{13}$$

The eq. (8.) with (9.) or (10.) can be used for resolving partly overlapping peaks.

The thermally stimulated discharge current method has effective frequency dependence on the activation energy and temperature range of transition. Although the determination of effective frequency has about 20% uncertainty, the effective frequency of these measurements are in the 10^{-3} Hz range.

$$\nu_{eff} = 0.113\frac{bA}{RT_m^2} \tag{14}$$

Biopolymers are not hard to investigate by depolarization method because of their polar nature. The polarization processes are quick, independent of the mobility of the polymer backbone. However, oxidative degradation and humidity can cause enough polar –C=O groups. Even the glass transition does not produce detectable depolarization current signal in the -110 - 125°C range. It must be mentioned that the depolarization currents and the relaxation strength values are at least two orders of magnitude smaller than in case of polar polymers, e.g. PVC [6].

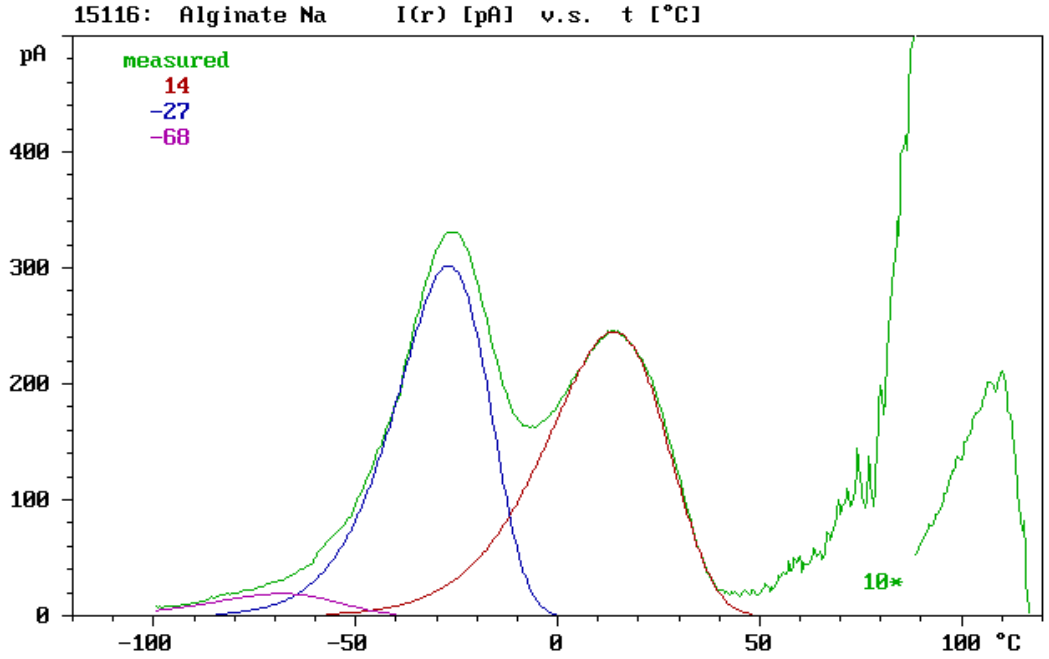

FIG. 7. NA-ALGINATE TSD CURVE BEFORE AND AFTER RESOLUTION

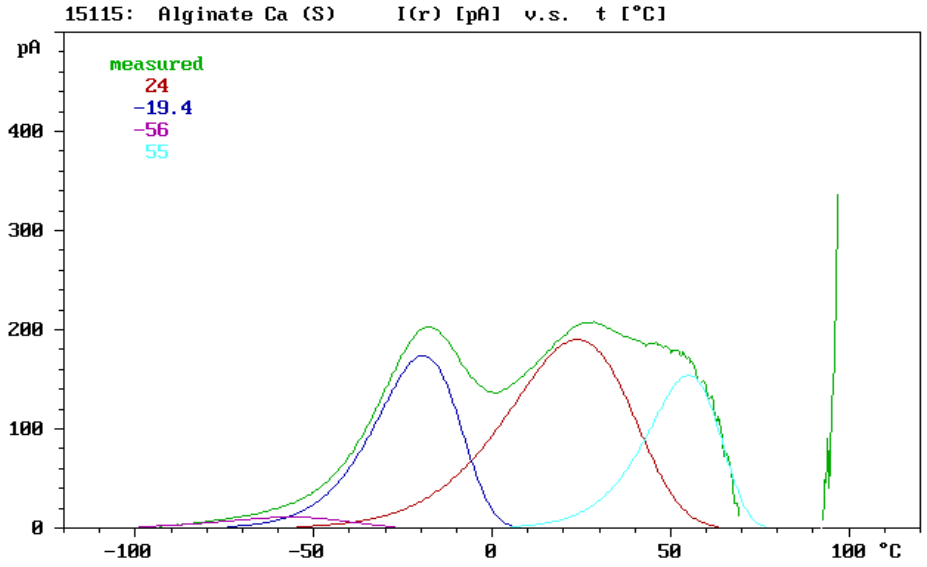

FIG.8. CA-ALGINATE TSD CURVE BEFORE AND AFTER RESOLUTION

Comparing the Na-alginate and Ca-alginate TSD curves, they show great similarity however after resolution of the Ca-alginate curve an extra peak appears in light blue colour at 55°C, which shows the effect of Na-Ca exchange, which influences the alginate polymer chains polarity.

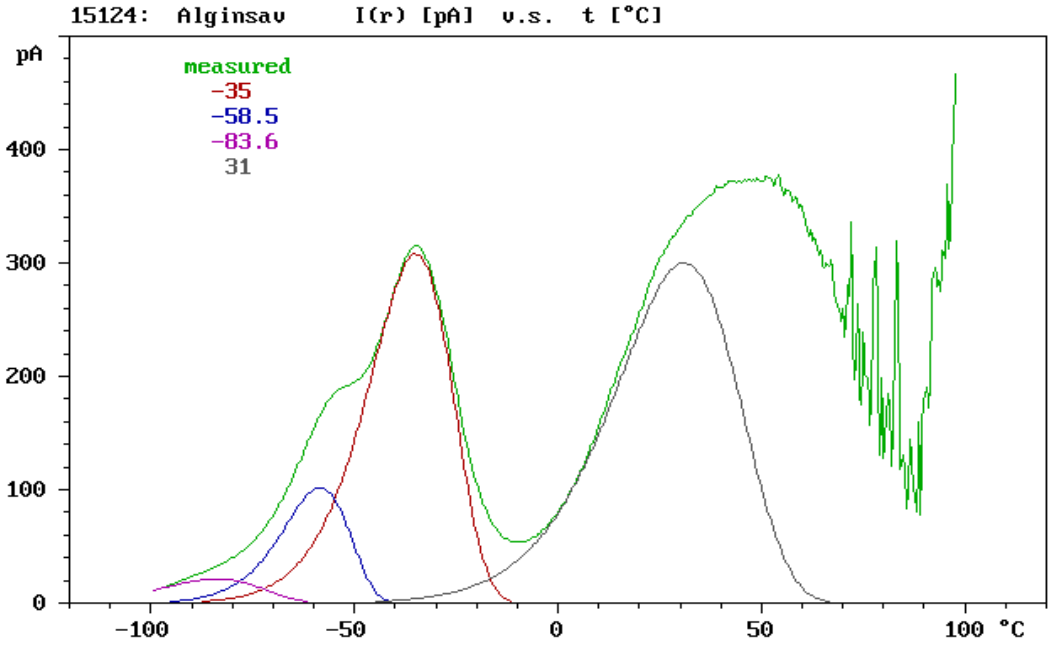

FIG.9. ALGINIC ACID TSD CURVE BEFORE AND AFTER RESOLUTION

When measured, the alginic acid's polarity was found to be significantly increased because of the alkyl group's appearance. The acid bath caused the replacement of Na ions to ethyl groups.

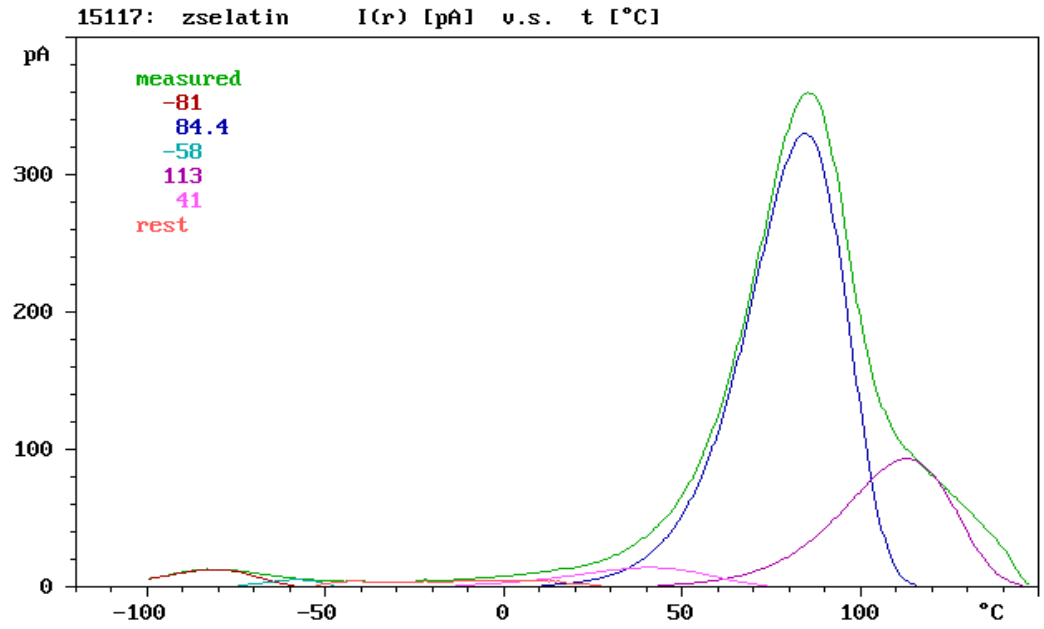

FIG.10. GELATIN TSD CURVE BEFORE AND AFTER RESOLUTION

According to the TSD curve the gelatin contains more polar components. The tests carried out have given a more accurate picture of the polar characteristics of each component a wider range of temperatures. The gelatin polarity depending on the origin of the gelatin-fish, bovine etc. gelaine.TSD spectra were resolved by our own software. Data of resolved transitions are summarized in Table 1.

TABLE 1
TSD RESULTS

Na-Alginate	**J_{max} [°C]**	**I_{max} [pA]**	**A_e [kJ/mol]**
1	14	245	44
2	-27	302	42
3	-68	19	21
Ca -Alginate	**J_{max} [°C]**	**I_{max} [pA]**	**A_e [kJ/mol]**
1	24	190	40
2	-19,4	174	44
3	-56	11	21
4	55	154	86
Alginic acid	**J_{max} [°C]**	**I_{max} [pA]**	**A_e [kJ/mol]**
1	16	302	78
2	-65	101	44
3	-82	11	21
4	29	298	86
Gelatin	**J_{max} [°C]**	**I_{max} [pA]**	**A_e [kJ/mol]**
1	-81	12,7	23
2	84,4	330	76
4	113	93	78
5	41	14	42

III. RESULTS

The aim of this work was to perform DSC and TSD measurements based on alginate and gelatin biofilms. The results of the DSC measurements show the importance of humidity, and water content of biofoils. Because of the similar structure and properties, it would be reasonable to try preparing biopolymer blends using alginate, gelatin or other gel forming bio materials. Glycerol like plasticizers may be also significant additives, as they can improve the mechanical properties, and the fracture resistance of the prepared films. The transformation of sodium alginate into Ca-alginate increases the mechanical strength, the thermal stability and decreases the water solubility of the alginate. The TSD measurements show that the biopolymers are easily detected because their polarity. Because of these properties the structure changes can be easily followed in case of polymer mixtures too. The polarity of the biopolymers could help in the application of adhesives and special solvents.

ACKNOWLEDGEMENTS

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