

Combined Mechanical and Electrical Study of Polymers of Biological Origin

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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 DMA method is used here to analyze the mechanical changes depend on temperature in biopolymers. 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 pectin 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 pectin and gelatin films was a single stage solving process.

1. 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 applications 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 structure line, artificial limb, 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.

Pectin is a structural heteropolysaccharide contained in the primary cell walls of terrestrial plants. It is mainly extracted from citrus fruits, and is used in food as a gelling agent, particularly in jams and jellies. It is also used in dessert fillings, medicines, sweets, as a stabilizer in fruit juices and milk drinks, and as a source of dietary fiber [2].

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 [3].



2. Experimental section

2.1. Materials

The biopolymer films were produced from pectin and gelatin (food additive) with different percentage of glycerol. For using casting techniques the following describes the method for each material. In the case of pectin and gelatin 2 m/m % aqueous solutions were made at room temperature, and drying in Petri dish in 35°C and 45% humidity. The films were then stored in desiccators 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 examine the movement of the molecules with DMA and TSD method.

2.2. Dynamic Mechanical Analysis

Dynamic mechanical analysis (abbreviated DMA) is a technique used to study and characterize materials. Dynamic Mechanical Test was carried out on strips cut from plates of about 1 mm thickness with Rheometrics Scientific MK-III instrument in dual cantilever mode at 1Hz frequency and 2°C/min heating rate. Glass transition temperatures were determined as the maximum temperature of mechanical loss factor ($\tan \delta$) maximum.

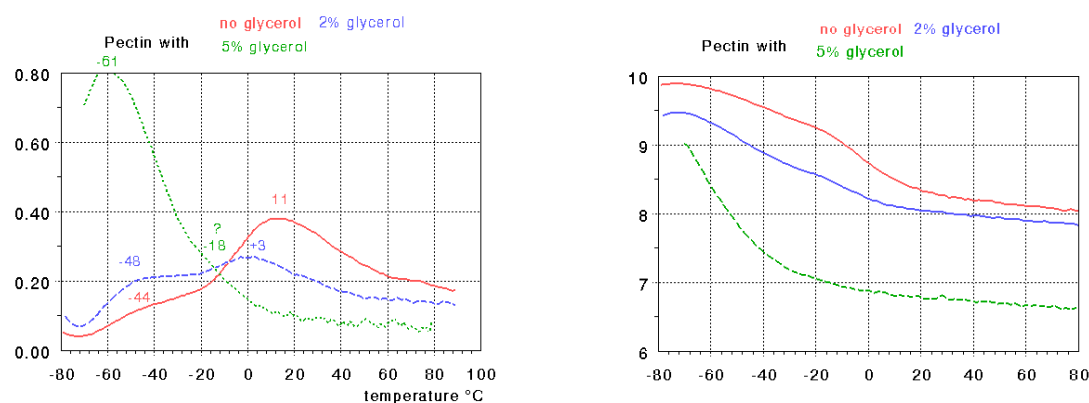


Figure 1. DMA curves ($\tan \delta$ left, E' right) of pectin

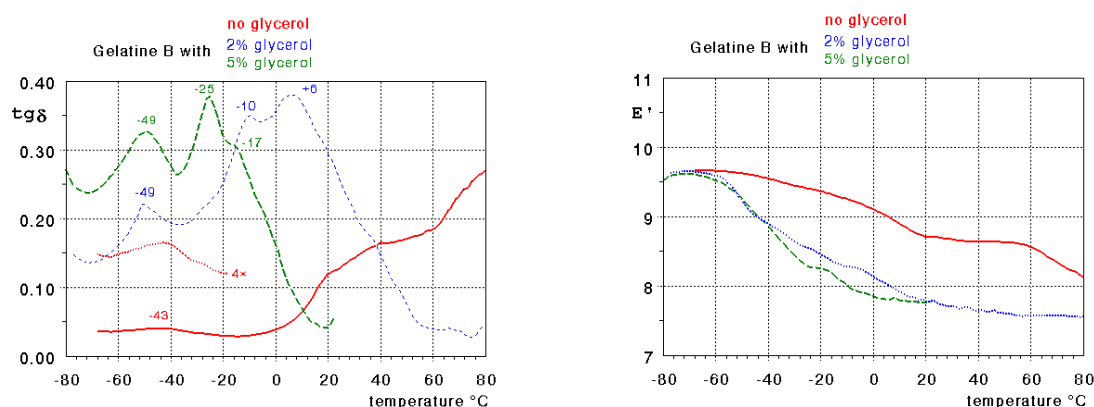


Figure 2. DMA curves ($\tan \delta$ left, E' right) of gelatin

Both pectin and gelatin (Fig. 1 and Fig.2) has multiple transitions in the investigated temperature range. Interestingly, the transition of lower temperature is not sensitive to presence of glycerol; the higher temperature ones are strongly dependent. The plasticizing effect is very strong for it.

In case of pectin the transition temperature goes below the transition temperature of low peak with 5% glycerol, the transitions are fused into each other.

In case of gelatin at least three transitions are present in the material. Similarly to the pectin the transition of lowest temperature is also almost independent of glycerol content. The high temperature transition is a doublet and the glycerol acts for both process. The peaks are unified without glycerol but split transitions are detected with even low, 2% glycerol concentration.

The nature of low temperature transition is still unknown.

2.3. Thermally Simulated Depolarization 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.
- Disk samples were used with sputter-coated gold electrodes
- Polarizing temperature: 125°C
- Polarization time: 10 minutes
- Polarizing field: 300 V/mm
- Cooling: 5K/min
- Start temperature: -150°C
- Heating rate: 5°C/min (after 10 minutes isothermal at -150°C)
- Final temperature: 125°C

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 curves. For the analysis of the depolarization processes the method is described in [4], 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

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

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:

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

the liberating charges produce current. The current density is

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

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

$$T = T_0 + bt \quad (4)$$

and the depolarization current density is

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

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

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

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 $A/RT \equiv s$

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

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:

$$A = 2.406R \frac{1}{\frac{1}{T_l} - \frac{1}{T_u}} \quad (8)$$

or both from the maximum and lower half

$$A = 1.443R \frac{1}{\frac{1}{T_l} - \frac{1}{T_m}} \quad (9)$$

and the maximum and upper half

$$A = 0.962R \frac{1}{\frac{1}{T_m} - \frac{1}{T_u}} \quad (10)$$

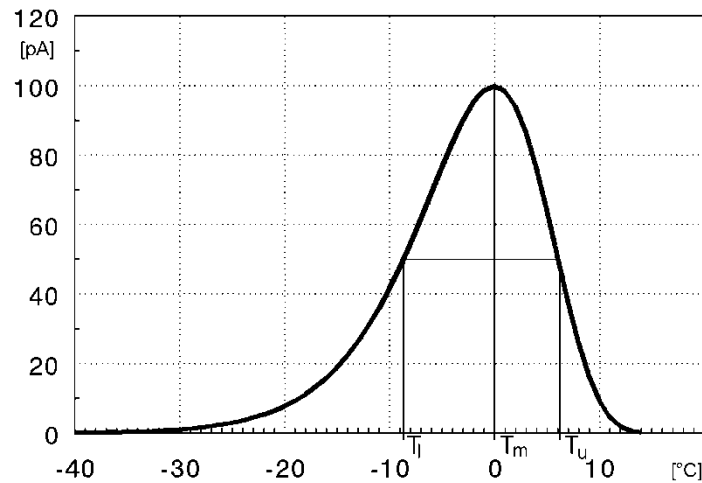


Figure 3. The shape of an ideal depolarization peak calculated by eq. (7) and the temperatures for determination of activation energy

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

$$\sigma = Q/A \quad (11)$$

The surface charge density can be used for determination of permittivity change of transition called oscillator strength (ϵ_0 - ϵ_∞)

$$\Delta\epsilon = \sigma/E\epsilon_0 \quad (12)$$

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

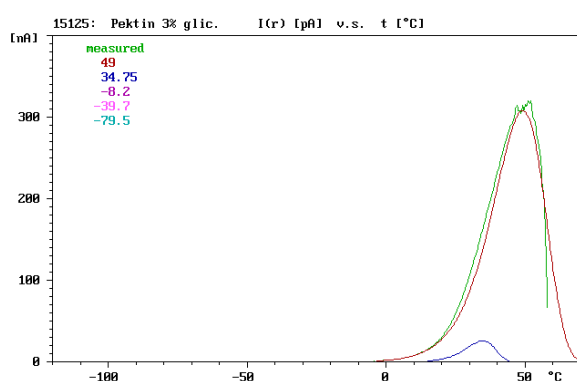
(13)

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.

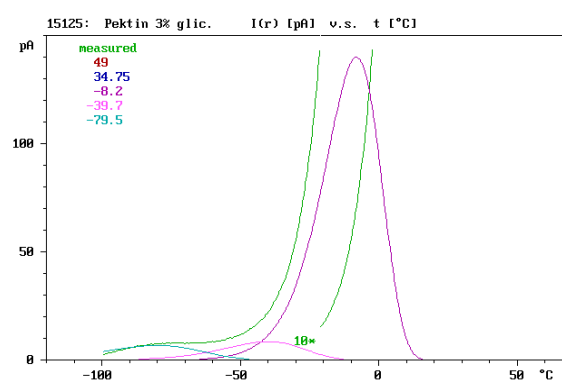
(14)

Pectin has two extremely intensive peaks in the 0-50°C range (Fig. 4 and 5). These peaks might origin from segmental movements but their intensity (I_{\max}) is amplified by ionic contamination. Because of the acidic nature of pectin, it contains free charge carriers. Low temperature peaks are also multiple ones showing independent molecular motions in the material.

twin process supporting the DMM results:



resolution



resolution (Low temperature peaks magnified)

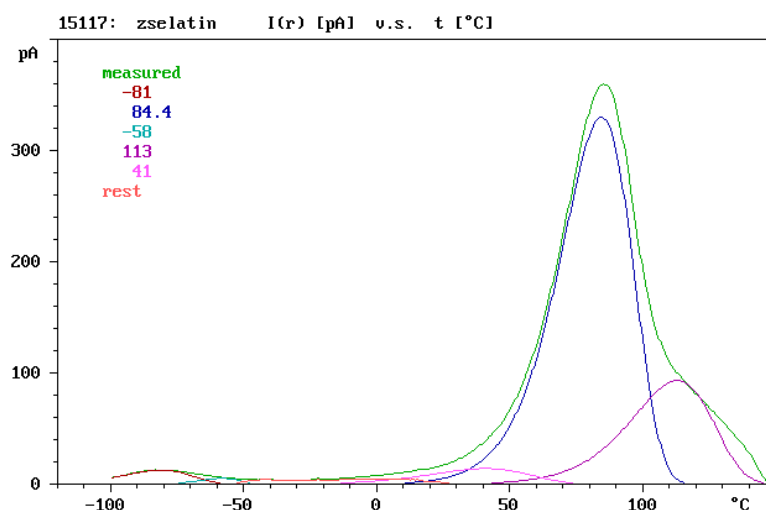


Figure 6. Gelatin TSD curve before and after resolution

TSD spectra were resolved by our own software. Data of resolved transitions are summarized in Table 1.

Table 1. TSD results of pectin and gelatin biofilms

Examined material; peaks	Peak location; ϑ_{\max} [°C]	Peak height; I_{\max} [pA]	Activation energy A_e [kJ/mol]
Pectin			
1	49	308000	72
2	34.75	25700	150
4	-8.2	140	55
5	-39.7	6.7	30
6	-79.5	6.7	16.5
Gelatin			
1	-81	12.7	23
2	84.4	330	76
4	113	93	78
5	41	14	42

3. Summary

The aim of this work was to perform DMA and TSD measurements pectin and gelatin biofilms. Both techniques revealed that these bio-materials have multiple transitions in the -120 – 80°C temperature range. These transitions are completely different in terms of compatibility with very polar plasticizer, namely the glycerol.

The difficulty of DMA method is that we work at the lowest force limit of the instrument because thin films can be produced only.

The TSD requests thin film specimens, but the method is sensitive to ionic contaminations. The resolving power of TSD is excellent. Using plasticizing additives of different polarity, we intend to

identify the nature of the transitions found. Both methods are suitable for these investigations and well complement each other.

References

- [1] *Handbook of Materials for Medical Devices*, ASM International 2003
- [2] Braconnot, Henri: "Recherches sur un nouvel acide universellement répandu dans tous les végétaux" (Investigations into a new acid spread throughout all plants) 1825 *Annales de chimie et de physique*, series 2, **28** 173-178.
- [3] *Gelatin Manufacturers* Institute of America: Gelatin Handbook 2012
- [4] K. Marossy, "Assessment of activation energies of transitions by thermally stimulated discharge current (TSD) experiments" 1989 *Polymer Bulletin*, vol. 22, pp. 213-220