Use of heat flows from DSC curve for calculation of specific heat of the solid materials

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Abstract

On basis of the second law of thermodynamics, has established a procedure for calculating the specific heat of solid materials using heat flow in the sample studied, and the rate of heating of the sample. Heat flow is obtained from DSC curve, the portion of the curve that does not cause thermal effects and gravimetric effects. For example, the specific heat has been calculated for lysozyme (globular protein) in the temperature range 139-190 ^{o}C, when the measurements were made in air and argon. Specific heat values of solid organic material are of great interest in the stability and functionality of the material.

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1. Introduction

Currently, there is a great interest for the study of thermal properties of materials, interest justified to their use in different environmental conditions, but being the components of plants operating in extreme conditions. The study builds on the principles of thermodynamics, but appeals and at driving force of bodies controlling the thermal properties and thermal phenomena in which they take part, namely the thermal agitation. Thermal motion of the ions, atoms and molecules of the solid, derived from its thermal energy.

2. Heat capacity and specific heat of the solid materials

The heat capacity of a body is heat exchanged with the outside of the body under certain conditions when the temperature changes by one degree centigrade. In most cases, the heat capacity of the solids to be confused with the heat capacity at constant volume (C_V), even though that which is determined experimentally, is the heat capacity at constant pressure (Cp). The difference of heat capacity at constant pressure and heat capacity at constant volume is relatively small and can be neglected especially at the lower temperatures than room temperature.
For metals, the heat capacity at constant volume is expressed in terms of energy oscillators of lattice nodes, and the energy of free electrons. According to the first law of thermodynamics, completed with the second principle of thermodynamics:

$$\delta Q = dU - dL = dU + pdV = TdS \tag{1}$$

At constant volume $dV = 0$, and C_V is written:

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \tag{2}$$

where: *S* is entropy of the system; *U* - its internal energy; *T* – temperature.
The heat capacity at constant pressure *Cp* is given by:

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p \tag{3}$$

where H is the enthalpy of the system.
The amount of heat that must to change it unit mass of material, for changing the temperature by one degree is called the specific heat, denoted by c:

$$c = \frac{1}{m} \frac{\delta Q}{dT} \tag{4}$$

The heat quantity exchanged by a body with mass *m* and specific heat *c(T)* for the temperature change from T_1 to T_2 is:

$$Q = m \int_{T_1}^{T_2} c(T) dt \tag{5}$$

3. Calculation of the specific heat at constant pressure from the DSC curve

Heat capacity and specific heat, and their variation with temperature can be determined by both methods, DTA and DSC, but generally the preferred method is DSC, which in this case provides greater accuracy.
The variation of the heat capacity with temperature different is produced in a crystalline solid characterized by a melting temperature T_t and a non-crystalline solid characterized by the glass transition temperature T_g. The heat capacity can be determined by the dimensional relationships, dividing the flow of heat from the heating rate of the sample:

$$\frac{\frac{\Delta Q}{\tau}}{\frac{\Delta T}{\tau}} = \frac{\Delta Q}{\Delta T} = C_p \tag{6}$$

Formula (6) can be written with the help of the heat flow, physical quantity which is obtained directly from the DSC curve.

Specific heat capacity is calculated using the formula [1]:

$$c_p = \frac{1}{m} \frac{\delta Q}{\Delta T} = \frac{1}{m} \frac{\left(\delta Q / d\tau \right)}{\left(dT / d\tau \right)} \tag{7}$$

In Eq. (7), the $(\delta Q/d\tau)$ is the heat flux given by the DSC curve, m is the sample mass and $(dT/d\tau) = \beta$ is the heating rate of the sample.

The necessary condition to determine the specific heat of a substance using the flow of heat is that the substance is stable in the entire temperature range in which is calculated the specific heat.

4. Determination of the specific heat at constant pressure of a protein using the heat flow from DSC curve

Using the method described above was determined the specific heat of lysozyme. Lysozyme is a globular protein consisting of amino acids (129 in humans). This protein (Fig.1), was discovered by Alexander Fleming in 1922.

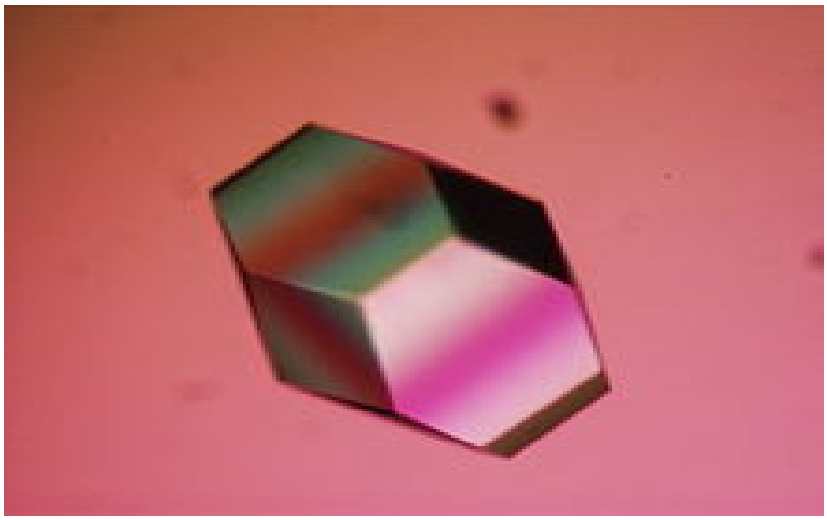

Fig. 1 Crystal of lysozyme

Lysozymes, also known as muramidase or N-acetylmuramide glycanhydrolase, are glycoside hydrolases. These are enzymes that damage bacterial cell walls by catalyzing hydrolysis of 1,4-beta-linkages between N-acetylmuramic acid and N-acetyl-D-glucosamine residues in a peptidoglycan and between N-acetyl-D-glucosamine residues in chitodextrins. Lysozyme is abundant in a number of secretions, such as tears, saliva, human milk, and mucus. It is also present in cytoplasmic granules of the polymorphonuclear neutrophils (PMNs). Large amounts of lysozyme can be found in egg white. C-type lysozymes are closely related to alpha-lactalbumin in sequence and structure, making them part of the same family. In humans, the lysozyme enzyme is encoded by the *LYZ* gene [2,3].
The enzyme functions by attacking peptidoglycans (found in the cell walls of bacteria, especially *Gram-positive* bacteria) and hydrolyzing the glycosidic bond that connects N-acetylmuramic acid with the fourth carbon atom of N-acetylglucosamine. It does this by binding to the peptidoglycan molecule in the binding site within the prominent cleft between its two domains. This causes the substrate molecule to adopt a strained conformation similar to that of the transition state [4]. According to Phillips-Mechanism, the lysozyme binds to a hexasaccharide. The lysozyme then distorts the fourth sugar in hexasaccharide (the D ring) into a half-chair conformation. In this stressed state, the glycosidic bond is easily broken.
Thermoanalytical measurements on the lysozyme were carried out on a horizontal „Diamond" TG/DTA analyzer from PerkinElmer Instruments, in dynamic air and argon atmospheres, using aluminum crucible. Heating was done with rate of 10 K min^{-1} from RT, to

1000 °C. The sample heated in air had a weight of 2.807 mg and the sample heated in argon had a weight of 2.221 mg.
In the figures 2 and 3 are represented TG, DTG, DTA and DSC curves, for the experiments carried out in air (Fig. 2) and argon (Fig. 3).

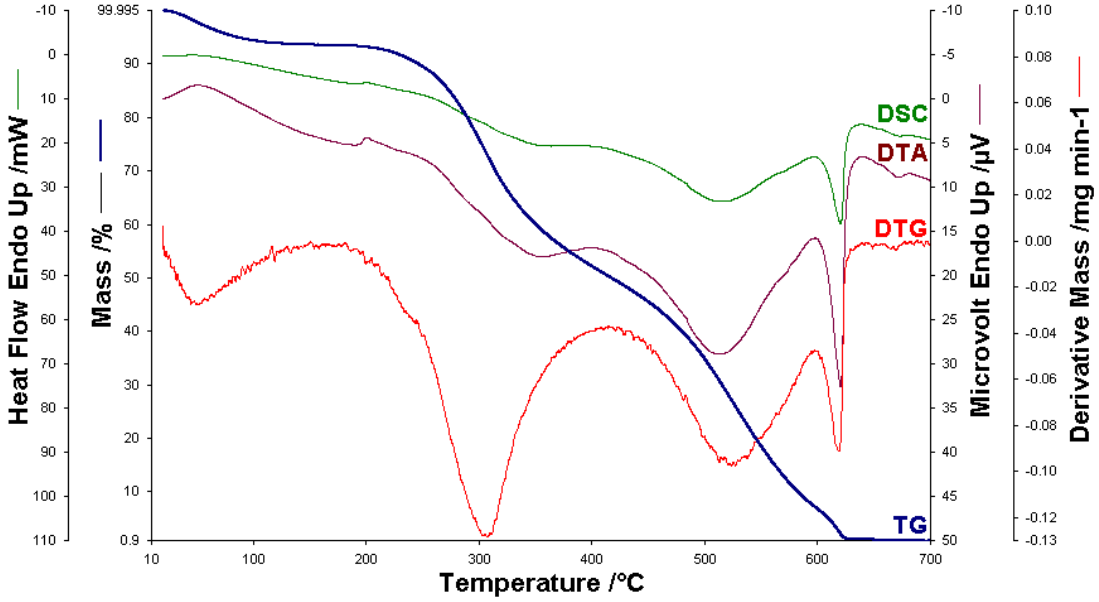

Fig. 2 Thermoanalytical curves of lysozyme in air

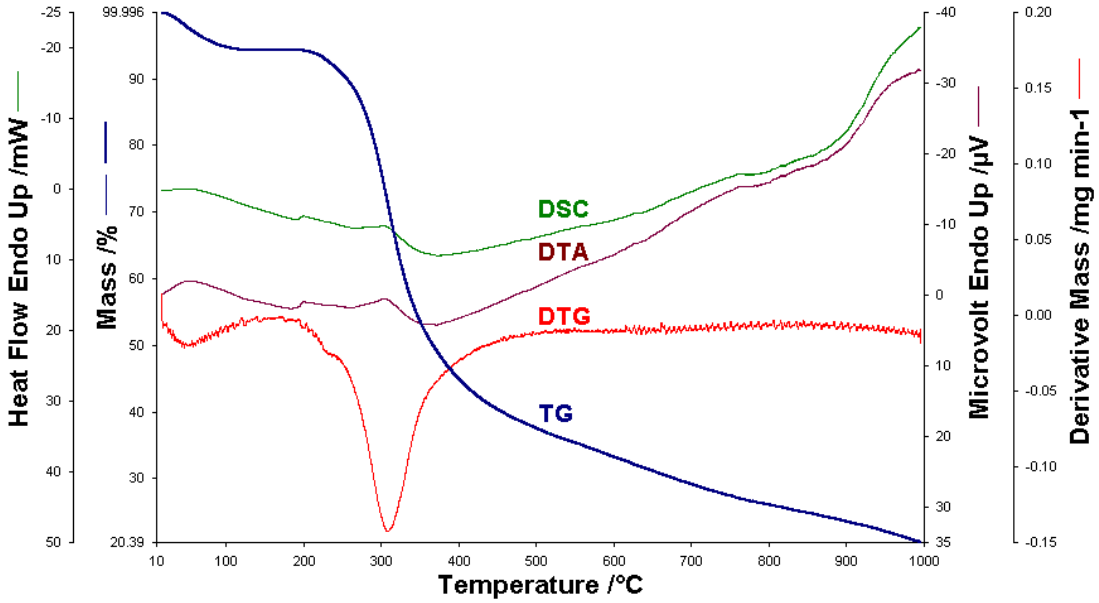

Fig. 3 Thermoanalytical curves of lysozyme in argon

In the air (Fig. 2), lysozyme has a mass loss of 6 %, and an endothermic effect, up to 130 °C. Then its weight remains constant up to 200 °C, until the thermal effect it is zero. At temperatures greater than 200 °C, lysozyme total decompose in three steps, all highly exothermic. Decomposition is total at 615 °C.

In the argon (Fig. 3), lysozyme has everything a mass loss of 6 %, and an endothermic effect, up to 130 ^{o}C. Then its weight remains constant up to 200 ^{o}C, until the thermal effect it is zero. At temperatures greater than 200 ^{o}C, the non-oxidative decomposition occurs. From 200 ^{o}C to 370 ^{o}C the decomposition is endothermic, and after 370 ^{o}C the decomposition is continuous and is not accompanied by thermal effects. At 1000 ^{o}C leave a residue of 20.4 %, but the thermal decomposition is not completed.
For the measurements shown in Figs. 2 and 3, have been identified the areas of stability of the mass, and the absence of heating effects, between the temperatures 130-190 ^{o}C.
As in other papers [5-7], by using heat flow from DSC curve with equation (7) has been calculate the specific heat of lysozyme in air and argon (Fig.4).

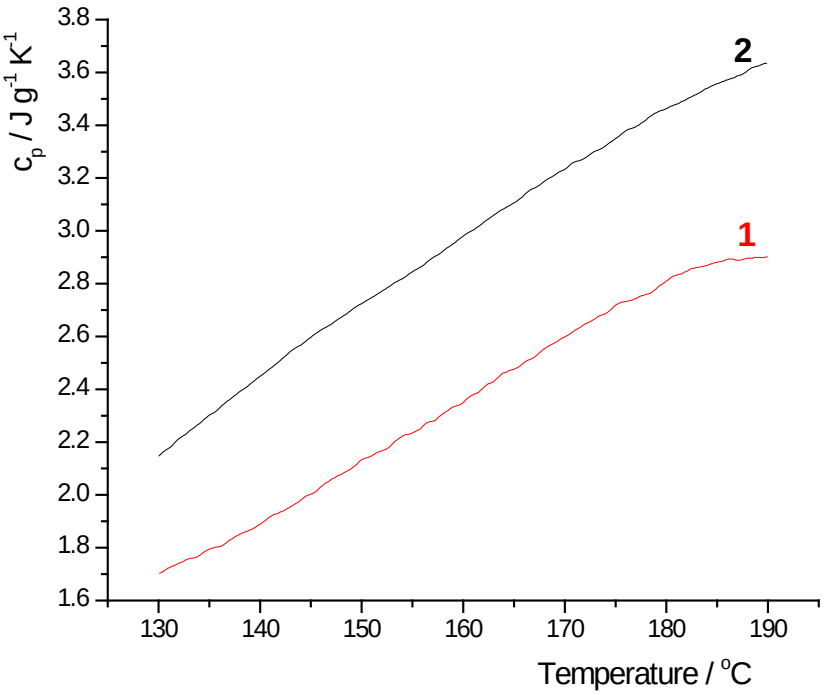

Fig. 4 The specific heat of the lysozyme: 1 – in argon, 2 – in air

5. Conclusions

The method for calculating the specific heat of the solid materials using the values of the heat flow curve of DSC proved to be accurate and easy to apply. It is accessible in all cases when is obtained DSC curve and measurement purposes is not necessarily the specific heat calculation.

References

1. Pop V, Chicinas I, N. Jumate N. Material Physics. Experimental Methods. Cluj-Napoca Romania: Presa Universitara Clujeana House; 2001.

2. Yoshimura K, Toibana A, Nakahama K. Human lysozyme: sequencing of a cDNA, and expression and secretion by Saccharomyces cerevisiae. *Biochem Biophys Res Commun.* 1988;150(2):794–801.

3. Peters CW, Kruse U, Pollwein R, Grzeschik KH, Sippel AE. The human lysozyme gene. Sequence organization and chromosomal localization. *Eur J Biochem.* 1989;182(3):507–16.

4. McKenzie HA, White FH. Lysozyme and alpha-lactalbumin: structure, function, and interrelationships. *Adv Protein Chem.* 1991;41:173–315.

5. Degeratu S, Rotaru P, Manolea G, Manolea HO, Rotaru A. Thermal characteristics of Ni–Ti SMA (shape memory alloy) actuators. *J Therm Anal Calorim.* 2009;97:695-700.

6. Harabor A, Rotaru P, Harabor NA. Thermal and spectral behavior of (Y,Eu)VO_4 powder. *J Therm Anal Calorim.* 2013;111:1211-9.

7. Degeratu S, Rotaru P, Rizescu S, Bîzdoacă NG. Thermal study of a shape memory alloy (SMA) spring actuator designed to insure the motion of a barrier structure. *J Therm Anal Calorim.* 2013;111:1255-62.