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Changes in polymer foils used in food packaging tested by using differential scanning calorimetry

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Abstract. This work is an experimental study of the differential scanning calorimetry characterisation of polymer materials used in food packaging materials, such as polypropylene (0·03 mm), polyethylene (0·1 and 0·03 mm), poly(D-(-)-β-hydroxybutyrate) (powder), two-layered polypropylene (0·064 mm), and two-layered polypropylene with poly-vinylidene-chloride (0·012/0·021). The polymer stability was checked by simulation of conditions during food preparation in microwave ovens, sterilisation or rapid freezing.

The materials were tested in the temperature range from 40 to 200°C at different scan rates from 2 to 30°C min^{-1} during heating or cooling. The enthalpies show a high correlation coefficient (0·964) with scan rate. All samples undergo phase change in the temperature range from 107 to 173°C during heating and enthalpies are in the range from 31·8 to 71·1 J g^{-1}. Upon subsequent cooling from 200°C, the temperature range of phase changes is shifted to lower temperatures from 86 to 102°C with enthalpies ranging from 30·4 to 57·8 J g^{-1}.

Experiments with exposure of polymers to microwave radiation and freezing prove that the phase change considering the temperature range is very similar in all experiments.

Keywords. Differential scanning calorimetry; polymers; food packaging; enthalpy; phase change.

1. Introduction

Packaging of food should prevent loss of nutrition, and prevent physical, chemical and biochemical reactions that deteriorate the quality of the packed food. Also, it should prevent any kind of contamination by microorganisms, insects, rodents and the like, or contamination by extraneous materials. Polymer materials used in food packaging are not absolute barriers against water vapour, gases or organic substances (Rellmann & Schenck 1992; Franz 1995; Johanson & Lavfven 1995). The sensory quality of the food, in particular the taste and flavour, is the most important criterion from the consumers' point of view (Werlein 2001).

The dependence of permeability on orientation is relatively slight and is due mainly to a decrease in diffusivity with orientation rather than to change in solubility in a fully glassy polymer. However, if there is some crystallinity present the added constraint on molecular

freedom in the non-crystalline phase leads to more efficient molecular orientation and to significant fall in permeation rates. The crystals can be regarded as essentially impermeable. In reality, the presence of the crystallites reduces the mobility of the polymer chains close to crystal boundaries, so that in the interfacial region the glass transition is effectively raised. By using thermal measurements via differential scanning calorimetry (DSC), the glass transition temperature (Tg) and the thermal stabilities of the polymers can be characterised (Hoekstra *et al* 1995; Khanna *et al* 1995; Gajdoš *et al* 2001). The crystallinity also defines the physical characteristics of the material such as the stability in different processes (Bonnet *et al* 1998; Demertzis & Franz 1998; Fuchs *et al* 1998; Plummer *et al* 2001; Zhu & Yan 2001).

The most commonly used polymer foils for food packaging are polypropylene and polyethylene. A large number of factors influence the barrier properties of packaging materials, both in the food itself and in the environment, like water vapour, gases and organic substances. High stability of the polymer foils is desired and great demand exists for use of stable materials in food packaging. It is preferable to know how the foils react under different conditions like heating or sterilisation and freezing because these are the treatments for preservation that may be used in a household (like exposure to the radiation in the microwave oven or freezing in the deep freezer).

Enthalpy, as a measure of the energy state of a system, can indicate if the polymer material is liable to stability change. These stability changes could also be indicators of possible loss of nutrient quality by using materials that do not adequately protect the food (Scheid 1968; Gajdoš *et al* 1996, 2001). For a number of polymer systems, for example, fatty foods in direct contact with plastic wrapping, the migration of substances from the polymer is governed by the amount of penetrant entering the polymer. For food packaging this means that the rate of migration of substances into the food can be governed by the uptake of food into the packaging itself (Harding *et al* 1997; Pentimalli 2000).

DSC measures the amount of energy absorbed or released by a polymer foil as it is heated, cooled or held at a constant temperature. Combined with the precise measurement of the sample temperature, DSC provides a nearly complete assessment of the chemical reaction or phase transformation taking place. The objective of this work is to show that polymer materials used for food packaging are in correlation with different conditions whom they are exposed. This study is not enough to assure prevention of eventual negative migrations or loss of food quality by using polymer materials as food packaging. However, it shows that stability experiments using DSC alone cannot prove the suitability of the packaging materials. It shows also the necessity of extension of scientific research in this field, because the storage of packed food under irregular conditions, according to the results presented in this study, can perhaps cause some undesirable side-effects that could lower the nutrient quality of packed or packaged food.

2. Materials and methods

A list of studied (commercially available) materials with their thicknesses and abbreviations, i.e. polypropylene (PP), co-extruded polypropylene (coex.PP) and polyethylene (PE), is given in table 1.

2.1 *Differential scanning calorimetry (DSC)*

The measurements were made on a Perkin–Elmer DSC-7 instrument. All polymer foils were cut into small discs of 7 mm diameter. The polymer discs were pressed into aluminium pans

Table 1. Polymer foils used in experiments.

Material	Abbreviation	Thickness (mm)
Polymer foil		
Polypropylene	PP	0·03
Polyethylene	PE	0·1 & 0·03
Poly(D-(-)-β-hydroxybutyrate)	PHB	powder
Multi-layered foils		
Polypropylene with polyethylene	PP/PE	0·064
Polypropylene with polypropylene with polyvinylidenechloride	PP/PP with PVDC	0·012/0·021

($d = 7$ mm, $h = 1{\cdot}5$ mm) that sealed were then with aluminium lids. The sum of the masses of the filled pan with the lid was 26 mg, and the average mass of samples was 20 mg. The samples were heated from 40°C to 200 and 340°C at a rate of 10°C/min, with an isothermal step at the highest temperature for 1–10 min. The process was continued with a negative scan rate of −10°C/min until the initial temperature was reached. All experiments were conducted under a purge of nitrogen.

Simulation of conditions during food preparation was conducted followed by checking the stability of the polymers. Simulation of cooking in a microwave oven was done by exposure to electromagnetic radiation during cooking of the polymer foils in a microwave oven for 1–10 minutes. This was then analysed by using DSC. In simulation of conditions during food sterilisation, the samples were heated thermostatically at a controlled temperature of 121°C for 5 to 10 min. In an experiment that simulated rapid freezing, samples were frozen with liquid nitrogen at −196°C, and then the heat flow was analysed by using DSC.

2.2 *Enthalpy determination*

Determination of enthalpy as a measure of the energy state of a system was determined from the DSC measurement curve (figure 1) by the integral equation (1) and compared with the

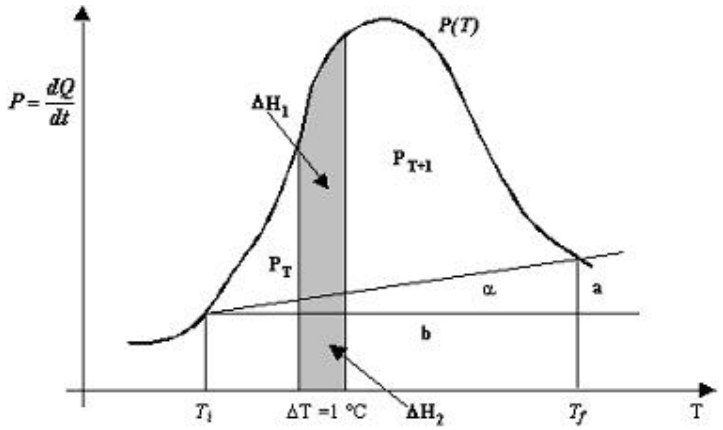

Figure 1. Numerical determination of enthalpy from DSC curves.

calculations using the trapezium rule according to (2). The trapezium rule describes heat flux between initial and final temperature of phase change (Gajdoš *et al* 1996, 2001).

$$\Delta H = \frac{1}{mr} \int_{T_i}^{T_f} \left[Q(T) - \frac{Q_i \left(T_f - T\right) + Q_f \left(T - T_f\right)}{T_f - T_i} \right] \mathrm{d}T, \tag{1}$$

where H = enthalpy ($\mathrm{J\,g^{-1}}$); Q = heat flux (mW); Q_i = initial heat flux (mW); Q_f = final heat flux (mW); T_i = initial temperature (K); T_f = final temperature (K).

$$\int_{x_0}^{x_n} y(x)\mathrm{d}x \approx \frac{1}{2} h \left[y_0 + 2y_1 + \cdots + 2y_{n-1} + y_n \right]. \tag{2}$$

To calculate the area under the curve (enthalpy), the curve was divided into segments with the initial value at temperature T_i and the end of the segment T_f, in steps of 1°C (ΔT).

The trigonometry function of angle a is defined as the tangent of α where P presents the heat flow Q in time t. Considering the equation of total enthalpy and also the mass, $\Delta H\,(\mathrm{J\,g^{-1}})$ and inserting all the parameters in one equation, the final equation for calculation of enthalpy from presented DSC curves is,

$$\Delta H = \frac{6}{m} \left[\frac{1}{2} \left[P_T + P_{T+1} \right] - \left[P(T_i) + \left(T + \frac{1}{2} - T_i \right) tg\alpha \right] \right], \tag{3}$$

where H = enthalpy ($\mathrm{J\,g^{-1}}$); PT = heat flux in time on the start of the segment ($\mathrm{mW\,}t^{-1}$); P_{T+1} = heat flux in time on the end of the segment ($\mathrm{mW\,}t^{-1}$); T_i = initial temperature (K); T = temperature at the start of the segment (K).

3. Results and discussion

Figure 2 is an overlay diagram of DSC curves of polyethylene for different scan rates in the temperature range from 40 to 200°C. The scan rates were varied for heating or cooling

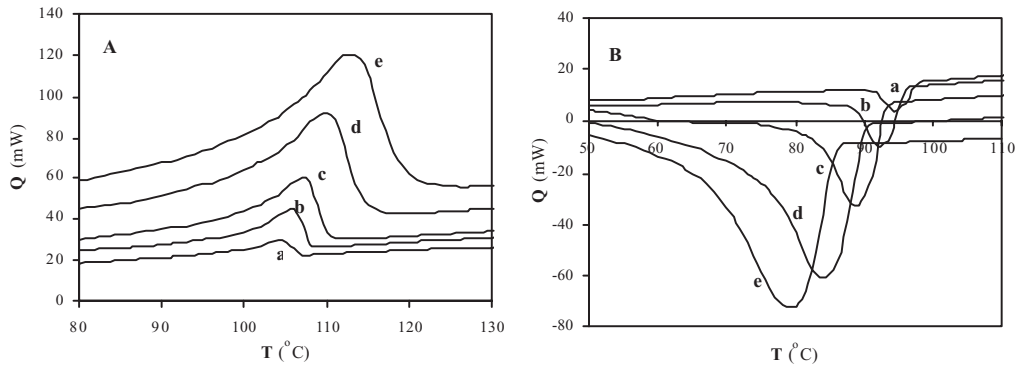

Figure 2. DSC diagram of PE (0·03 mm) foil with increase **(A)** and decrease **(B)** of temperature at different scan rates. The scan rates of decreasing and increasing temperatures are (a) 2, (b) 5, (c) 10, (d) 20 and (e) 30°C $\mathrm{min^{-1}}$.

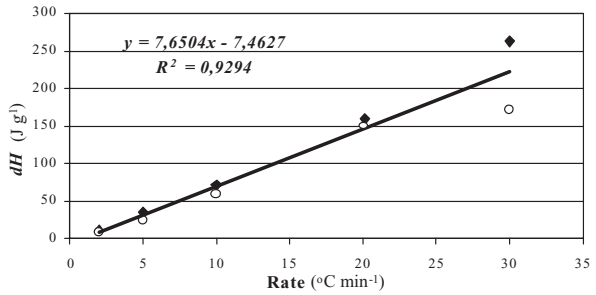

Figure 3. Differential scanning calorimetry (DSC) data for crystallisation enthalpy of PE (0·03 mm), ΔH as a function of heating (♦) and cooling rate (o).

cycles for polymer from 2°C per minute continuing with 5, 10, 20 and ending with 30°C per minute. Temperature was varied in a closed loop; at first with temperature increasing to attain the maximum temperature, followed by a step with constant maximum temperature, and continuing with temperature decrease to reach the initial value.

The obtained results are in a good agreement with that previously published (Gajdoš *et al* 1996, 2001; Janigova *et al* 2002). The initial and final temperatures as well as the associated heat flow of the phase change process were obtained by means of the points of intersection of the background line with the peak signal.

To show that enthalpy is a function of scan rate, the results of calculations of enthalpy, ΔH, (1) and (3), show a high correlation that proves the authenticity of the idea with a correlation coefficient of 0·964. Results of enthalpy are very similar using both methods that have been used in the calculation. From figure 3, it is proved that it is necessary to provide more energy in the transition from solid to fluid phase than is necessary in the opposite direction. It is obvious that an increase of scan rate also increases the difference between enthalpies of heating and cooling for a polymer foil.

The results presented (figures 4–5) were obtained in experiments with temperature increase starting from 40°C and a scan rate of 10°C min^{-1}. The samples undergo a phase change in the temperature range from 107 to 173°C with the enthalpies in the range from 31·8 to 71·1 J g^{-1}. Upon subsequent cooling from 200°C the temperature range of phase changes was shifted to lower temperatures from 30·4 to 57·8 J g^{-1} which is in good agreement with results previously published.

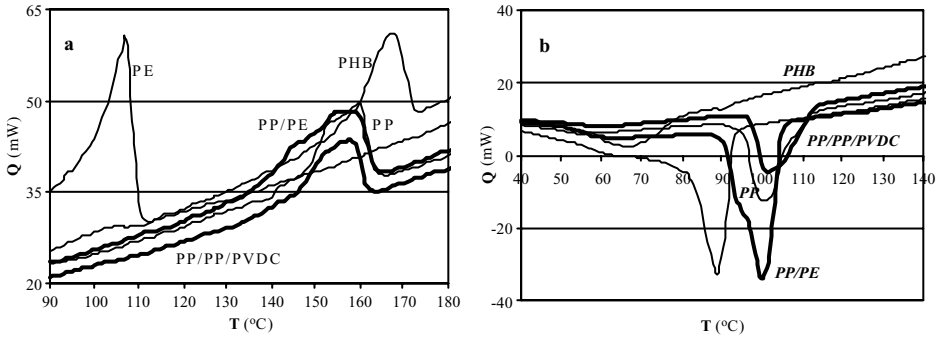

Figure 4. Differential scanning calorimetry (DSC) data for polymer foils, polyethylene, polypropylene, poly(D-(-)-β-hydroxybutyrate), and for multi-layered foils such as polypropylene with polyethylene and two-layered polypropylene with PVDC for increase **(a)** and decrease **(b)** of temperature at the scan rate of 10°C min^{-1}.

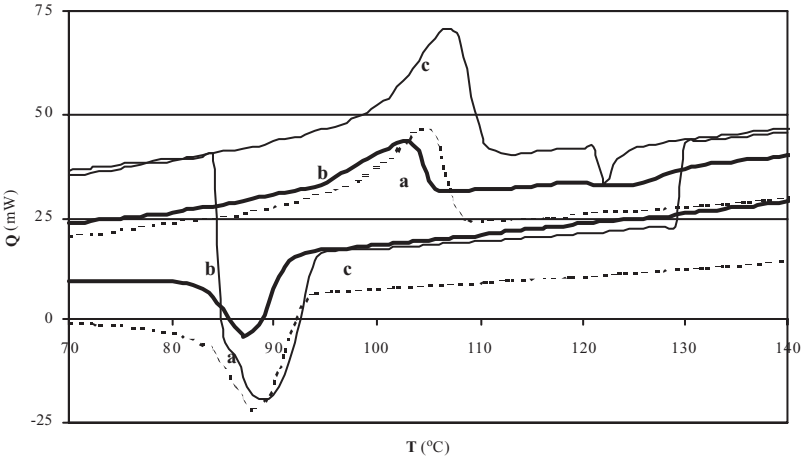

Figure 5. DSC diagram for polyethylene foil (PE, 0·03 mm) obtained by simulating exposure to microwaves (a), rapid freezing (b) and sterilisation process (c), at a scan rate of 10°C min^{-1}.

With simulation of sterilisation, the aim was to simulate conditions as was described by Briese (Briese *et al* 1994). The aim of simulations of microwave heating, freezing and sterilisation and observing the heat fluxes using DSC was to show that some unusual endothermic changes can perhaps cause some loss of food quality by migrations of the material or food.

The heat fluxes of polyethylene and polypropylene foils determined by DSC show the same shapes for the same scan rate exposed to different terms (figures 5 and 6). In figure 5 an unusual trend is seen in the flow for simulation of sterilisation process where the heat flow over 121°C shows a rapid drop (*c* in figure 5) which is also seen in figure 6. (*c* in figure 6). This can be explained as a endothermic decrease. This decrease can perhaps also enable some

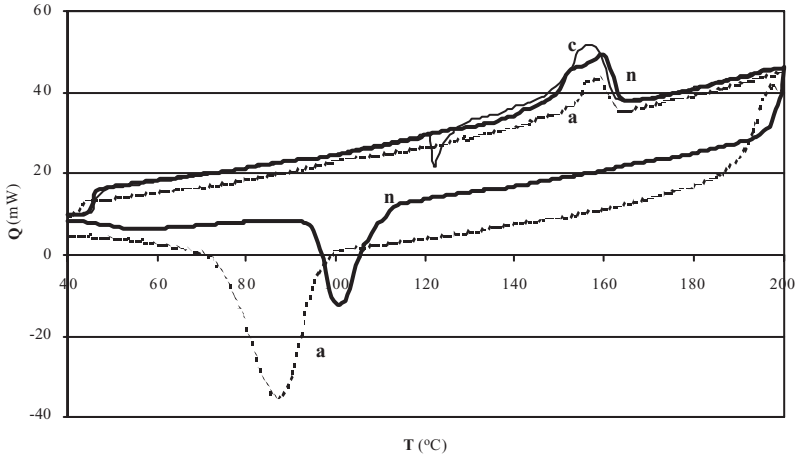

Figure 6. DSC diagram for polypropylene foil (PP, 0·03 mm) obtained by simulating exposure to micro waves (a), not exposed to any process (n) and sterilisation process (c), at a scan rate of 10°C min^{-1}.

migrations from the material or the food. An unusual heat flux for polyethylene is observed as temperature decreases (curve c on figure 5).

It is interesting is that the polypropylene foil shows endothermic decrease before the usual phase change (figure 6). Different processes were simulated to show differences in polymer behaviour. For PE, sterilisation and rapid freezing were simulated. The phase changes show increasing temperatures in the range 103–107° C, with enthalpies in the range $22\,J\,g^{-1}$ for the rapid freezing to $59\,J\,g^{-1}$ for the sterilisation process. Those results indicate that simulated processes have a larger influence on polymer stability than is expected from previously published results. However, the experiments on stability of polymer foils, used in food packaging using DSC alone, cannot prove the suitability of the packaging materials because other data like migration of material from and to it are also required in polymer foil evaluation. According to present results, it would be preferable to continue with measurements on polymer foils used as food packaging to determine if different processes of food preparation show any migration from the material in the food or vice versa, considering different heat fluxes of different simulating processes (figures 5–6).

The crystalline fraction obtained from the DSC measurement was calculated by $X_{c,DSC} = H_f/H_{f,c}$, with H_f the heat fusion ($71\,J\,g^{-1}$ and $37\,J\,g^{-1}$ for PE/0·03 mm and PP/0·03 mm) and $H_{f,c}$ the heat fusion for pure crystalline polyethylene material ($H_{f,c} = 287\,Jh^{-1}$) (Hoekstra 1996). The calculated $X_{c,DSC}$ value was 24·7% for the PE foil, which represents an intermediate degree of crystallinity (20–60%), a characteristic of low-density polyethylene (Billmeyer 1971).

4. Conclusions

The DSC measurements resulted in determination of the enthalpy temperatures of polymer phase change. The polymers tested showed great structural stability for temperatures up to 200°C.

The correlation coefficient (0·964) between enthalpy and scan rate for polyethylene shows that those two characteristics are highly connected. Experiments with exposure of polymers to microwave radiation and freezing show that the phase change over the temperature range is similar in all experiments, but change in enthalpy depends on the simulating process.

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