ELSEVIER
Thermochimica Acta 333 (1999) 87–93
thermochimica acta

DSC-Measurements of amber and resin samples

P. Jablonski[a], A. Golloch[b], W. Borchard[a,*]

[a]*Angewandte Physikalische Chemie, Institut für Physikalische und Theoretische Chemie der Gerhard-Mercator-Universität Duisburg, 47048, Duisburg, Germany*
[b]*Instrumentelle Analytik, Gerhard-Mercator-Universität Duisburg, 47048, Duisburg, Germany*

Received 3 March 1999; received in revised form 28 April 1999; accepted 28 April 1999

Abstract

In the present paper the thermal behaviour of amber and a resin of a pine tree has been investigated with the aim to show a correlation between the age of amber and its thermal behaviour. The thermal analysis of samples have been performed using a differential scanning calorimeter. After thermal analysis of the samples under different conditions the similarity of resin and amber relating to their thermal behaviour and their age is shown. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: DSC; Glass transition; Age of amber; Enthalpy relaxation

1. Introduction

So far there is no method known to determine correctly the age of amber which is derived from natural resins by a long ageing process. The age of the different types of amber is often differently indicated, since amber was mostly relocated before its final storage. The different chemical constitution of amber hinders additionally the exact determination of its age. The age of amber is often derived from inclusions of insects. The DNA of the insects has been used recently to find biological links in the evolution and by it the approximate age of the surrounding amber [1]. Other attempts using NMR techniques [2] or radiometric K/Ar measurements [3] only result in the approximate age of the amber samples. Furthermore the measurements should be carried out with one kind of amber of different ages which is in principle not realisable. It was the idea that thermal analysis of amber might give a chance to determine the age of the glassy solidified resins. Principally the glass transition of polymers and its dependence on their thermal prehistory and the experimental conditions can be used to determine their ages. It is known that polymers can be transformed into the glassy state and the transition from the glassy state to the liquid can be measured by differential scanning calorimetry. Depending on the thermal prehistory of the material, the measured DSC curves show characteristic forms which will be described in this paper. To compare the characteristic form and the age of the samples and to get a correlation between these two characteristics the amber samples of different ages and a 25-year-old resin taken from a pine tree were measured by means of a differential scanning calorimeter.

---

*Corresponding author. Fax: +49-203-379-2110.

PII: S0040-6031(99)00101-X

2. Theoretical aspects

2.1. The glass transition

The glass transition can be demonstrated by use of an isobaric enthalpy-temperature diagram. Fig. 1(a) schematically shows the enthalpy-temperature curve for a polymer that may crystallize or solidify into a glass under assumption of constant values of the specific heat capacity. Under certain conditions the polymer may crystallize at the melting temperature T_m or a little below it. As a consequence of melting a step results in the enthalpy-temperature curve. The magnitude of this step corresponds to the melting enthalpy of the polymer. If the crystallization of the polymer is suppressed by fast cooling the molecules cannot reach their equilibrium positions to crystallize and thus the polymer solidifies to a glass [4]. The enthalpy-temperature curve is linear above T_e which is the highest temperature of the freezing-in interval. Below this temperature the transition starts from the highly viscous supercooled melt into a rigid glass upon cooling. At T_e, the enthalpy-temperature curve deviates from the curve of the melt and joins the curve of the glass. Below T_{gl}, which is the lowest temperature of the freezing-in interval, the course of the enthalpy-temperature curve is again linear and is situated above the curve for the crystal state. The intersection of the linearly extrapolated curves of the melt and the rigid glass is defined as the glass transition temperature T_g [5]. In the glassy state the macro-Brownian mobilities are completely hindered and the micro-Brownian mobilities are partially frozen in. If the cooling rate decreases the beginning of the glassy solidification and T_g will shift to lower temperatures.

The specific heat capacity is characterized by a step in the $\tilde{c}_p(T)$ diagram which can be measured in a DSC experiment (Fig. 1(b)). In this case the curves were drawn when the cooling and the heating rate in a DSC experiment are the same and the polymer is not annealed at any temperature below the glass transition temperature T_g. For all other conditions the curve of the specific heat capacity as a function of temperature is different.

2.2. Dependence of the glass transition on the difference of cooling and heating rate

There are three cases to be discussed [4,6]. First of all when the cooling and the heating rates are the same. Secondly when the cooling rate is larger than the rate of heating and last when the heating rate is larger than the rate of cooling. In the first case when the cooling and heating rates are identical, DSC plots and enthalpy-temperature diagrams shown in Fig. 1(a,b) will result.

In the second case where the cooling rate is larger than the rate of heating, an exothermal peak in the

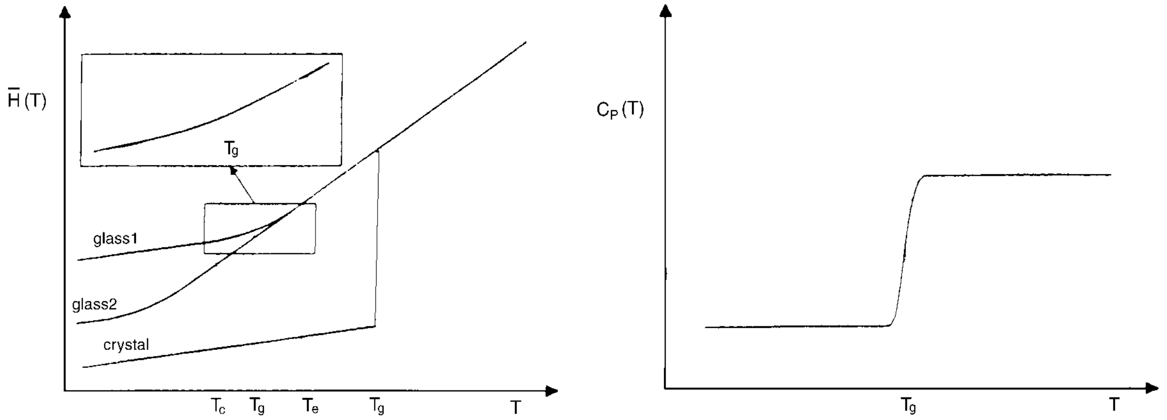

Fig. 1. (a) Enthalpy-temperature relation between glass melt and crystal schematically, glass 1 fast cooling, glass 2 slow cooling (T_m melting temperature; T_e beginning of freezing-in; T_{gl} end of freezing-in; T_g glass transition temperature). (b) Specific heat capacity as a function of the temperature in a schematical representation.

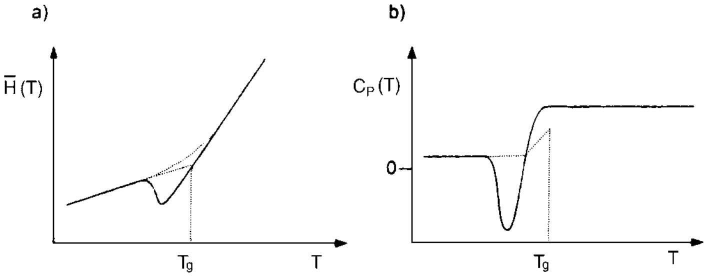

Fig. 2. Glass transition where the cooling rate is larger than the rate of heating schematically. (a) Enthalpy-temperature diagram; (b) specific heat capacity as a function of the temperature. c_p in arbitrary units.

DSC plot is observed. This is caused by relaxations in the polymer, a few degrees below T_g, during the heating process. From the enthalpy-temperature diagram it can be seen that the enthalpy decreases below T_g and reaches the linear extrapolation of the equilibrium curve of the undercooled melt. Because of the increased mobility of the polymer the system may achieve a state which is closer to the state of equilibrium conformation belonging to the temperature of the system. The measured exothermal peak is detected at temperatures lower than T_g (Fig. 2).

In the last case where the cooling rate is lower than the rate of heating, an endothermal maximum in the DSC plot may be observed (Fig. 3).

It is shown in the enthalpy-temperature diagram that the enthalpy curve follows the linear extrapolation of the glass curve at temperatures above T_g and reaches the equilibrium enthalpy curve of the melt at a higher temperature. The polymer cannot follow the equilibrium curve of the melt at T_g because the relaxation processes are slow relatively to the fast change of the temperature. There is an 'overheating effect' shown in the enthalpy-temperature diagram. The equilibrium curve of the melt is reached at a higher temperature and therefore the measured endothermal peak is detected at temperatures above T_g. The large differences of cooling and heating rates is better expressed as the endo- and exothermal maxima in the DSC plots.

2.3. Annealing of the polymer

If the polymer is cooled just a little below T_g and annealed at a defined temperature below T_g, for example T_a, relaxations in the polymer take place (Fig. 4) which may be discribed by a simple multiparameter model [7]. The polymer is in an impeded non-equilibrium state. The molecules oscillate mainly around their equilibrium positions without changing their places. Because of the micro-Brownian mobilities the enthalpy of the system decreases to the direction of the linear extrapolation of the equilibrium curve of the melt. After annealing and heating the polymer starting at low temperatures an endothermal maximum

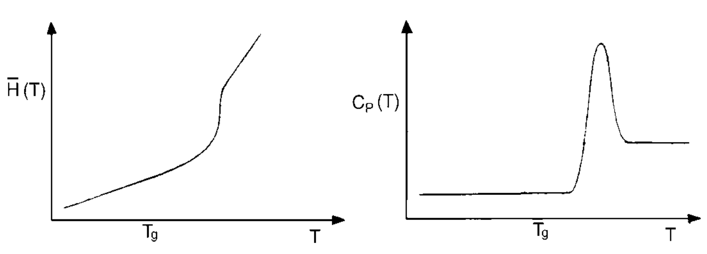

Fig. 3. Glass transition where the cooling rate is smaller than the rate of heating schematically. (a) Enthalpy-temperature diagram; (b) specific heat capacity as a function of the temperature. c_p in arbitrary units.

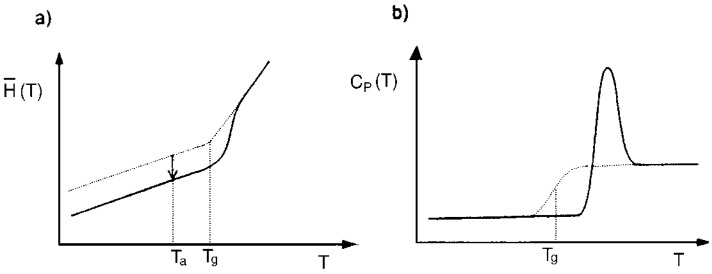

Fig. 4. Glass transition for annealed polymers in a schematic representation. (a) Enthalpy-temperature diagram; T_g glass transition temperature; T_a annealing temperature. (b) Specific heat capacity as a function of the temperature.

is measured like in the case where the heating rate is much larger than the rate of cooling. The magnitude of the peak depends on the annealing time and the annealing temperature which is below the glass transition temperature T_g. If the enthalpy of relaxation is large there will also be the large area of the measured peak in the DSC plot. This is realized if the annealing time is long and when the annealing temperature is only a few tenth K below the glass transition temperature. This correlation between annealing time and annealing temperature to the magnitude of the peaks offers a chance to determine the age of a glassy solidified polymer material by means of thermal analysis.

3. Experimental details

The amber samples were taken from the interior of three different slices of fossilized resins of different ages. The first amber sample was between 10 and 25 million years old and the second has an age of 40–60 million years, the third sample is between 70 and 135 million years old (Table 1).

All amber samples were pulverized in an achat mortar before the measurements to guarantee good thermal contact. The resin samples were taken from pieces of 25-year-old resins of a pine tree collected at Harz / Germany. The resin was taken from the surface of the pieces solidified to a glass. Amber and resin samples were measured using a differential scanning calorimeter (DSC-2C) from Perkin Elmer with a low temperature device to reach temperatures down to 85 K. The calibration of the temperature and the analysis of the linearity of the signal were performed using water and benzoic acid. The transition temperature was constructed by the linear extrapolation of the base-line and the linearly extrapolated left flank of the measured transition peak. The intersection of these two straight lines was set to the melting temperature. All samples of 10–14 mg were measured in high pressure steel pans purchased from Perkin Elmer. All glass transition temperatures were constructed using the method of Savill and Richardson [5].

Table 1
Age and number of used amber samples

Sample	Age in million years
1	10–25
2	25–60
3	70–135

4. Results

The process and transformation of a resin into amber is not fully understood but it is a fact that a young resin is soft and tacky and after polymerisation of organic compounds and/or the evaporation of volatile terpenes the resin will solidify to a glass and transform into amber. Natural amber has been annealed for million years eventually at several temperatures. Because of the long annealing time it is possible that the relaxational effects in the glassy solidified amber are strong and appropriate for the determination of its age.

In the DSC plots of the first run of amber, an exothermal minimum in the range from 350–450 K is obtained followed by a flat wide melting range up to

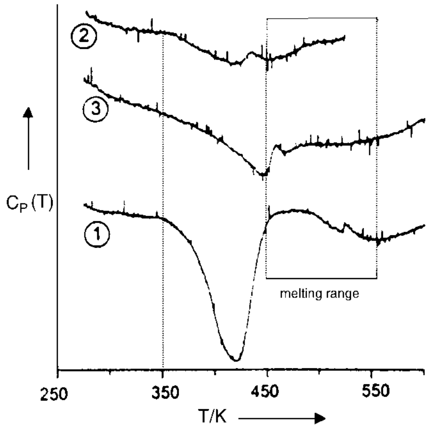

Fig. 5. DSC plots of amber samples (the 1st run), c_p in arbitrary units, see text.

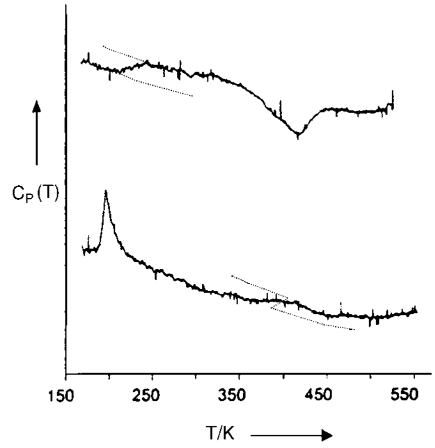

Fig. 7. DSC measurements of a resin. Upper curve for the 1st run; lower curve for the 2nd run, c_p in arbitrary units.

550 K which may consist of many single overlapping melting peaks (Fig. 5). The youngest amber sample (1) shows the largest exothermal effect. The magnitudes of the other two are similar. Related to the theory of annealed polymers there should be measured a large overheating effect which is charaterized by a large enthalpy of relaxation and therefore an endothermal maximum results in the DSC plot. After the first run the amber samples are cooled with a cooling rate of 5 K min^{-1} and repeatedly measured with a heating rate of 40 K min^{-1}. In the DSC plots of the second run (Fig. 6) it was found there are no more exothermal signals in the curve. Only glass transitions were detected between 350 K and 400 K. The youngest amber sample (1) shows the glass transition at the lowest temperature. Only in the DSC plot of amber sample (1) there is a small endothermal maximum detected below T_g. After annealing the samples 3 K below their glass transition temperatures for 48 h, the DSC measurements show the same course as the measurements in the second run. There are no enthalpy relaxations found.

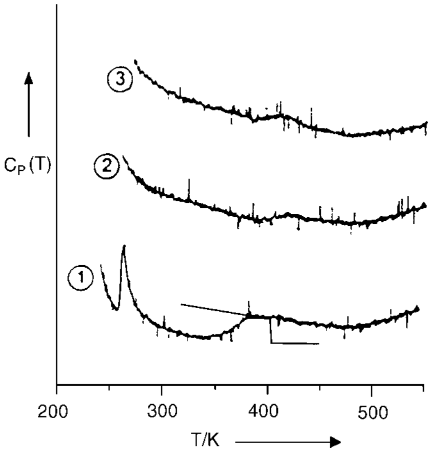

Fig. 6. DSC plots of amber samples (the 2nd run), c_p in arbitrary units, see text.

The analysis of the resin samples were also carried out to draw a comparison between the samples of amber and resin. The outside of the resin pieces are solidified to a glassy state and have been measured under the same conditions as the amber samples in two successive runs (Fig. 7). There is an exothermal peak at 400 K in the first run which is smaller than the exothermal peak measured in amber sample (1) but more pronounced than in the two old amber samples. In the DSC trace of the second run of the resin there is an endothermal peak at 200 K and a glass transition at 400 K. The glassy solidified 25-year-old resin samples show a thermal behaviour similar to the several million years old amber samples. In all samples an exothermal minimum is detected which is marked in young amber and in resin contrary to the expected endothermal maximum caused by the large enthalpy of relaxation. This exothermal minimum disappeared in the second run while glass transitions have been detected in the range from 350 K to 420 K. The transformation of resin into amber occurs in two effects running in parallel to each other. One effect is the polymerization of organic compounds in the resin the other is the diffusion of volatile compounds which takes millions of years. The comparison between the glassy solidified resin and the amber samples shows that during the diffusion of volatile compounds the viscosity and with it the glass transition temperature increases and ultimately the total resin solidifies into a glass at the surface although the interior of the sample remains in the state of a melt. After that the diffusion of the volatile compounds is impeded so there are volatile compounds left in the resin pieces. In the amber pieces there are also volatile compounds which cannot diffuse out of the pieces. It is known that the diffusion coefficients D in glassy materials are extremely small [8,9]. The mean squared displacement $\overline{x^2}$ being related to the time t in one direction is given by:

$$\overline{x^2} = 2Dt \tag{1}$$

If D is 10^{-11} $\mathrm{cm^2\,s^{-1}}$ in highly concentrated polymer solutions and even lower, for example 10^{-19} $\mathrm{cm^2\,s^{-1}}$ in glassy states, the time necessary to pass a distance of 1 cm is 1.6×10^3 years and 1.6×10^{11} years in a glass. This last time in this approximation is longer than the age of the oldest amber by factor 10^3. Therefore the amount of diffusable relatively low molecular material additionally depends on the thickness of the piece of amber.

This is also shown by the experiment where the amber is heated outside the DSC. During this heating process the amber melts and the evaporating substances smell like volatile terpens in resins.

Amber sample (1) shows an endothermal peak at 300 K in the second DSC run. This peak and the endothermal peak in the second run of the resin samples might belong to compounds which were left in the amber pieces and cannot crystallize, in amber and in resin, respectively. After the first run these compounds may crystallize so there results an endothermal maximum during the second run. Another explanation is also possible that by-products of an exothermal chemical reaction during the heating process were formed.

Although the conclusions have been drawn the determination of the age of amber by thermal analysis using the enthalpy relaxation is not possible. The variety of the chemical composition of different types of amber does not permit a comparison of the age and the thermal behaviour. Rehage and Borchard demonstrated this by means of the volume relaxation of polystyrene [4,10]. A measurable relaxation could only be reached by annealing the samples a few K below their glass transition temperatures. An annealing temperature of 12 K below the glass transition temperature requires an annealing time of 1 year. If the annealing temperature is 70 K below the glass transition temperature the relaxations will take more than 10^{34} years in a logarithmic extrapolation. Although this has to be regarded with caution the times are extremely long. An annealing temperature of about 100 K below the glass transition temperature like in the amber samples prevents all processes of relaxation. It should be possible that the relaxations in amber are faster than in polystyrene. Besides this the exothermal effects in the first run overlap with the glass transition resulting from the possible enthalpy relaxation found in the amber samples.

5. Conclusions

The aim of the present paper was to investigate the thermal behaviour of amber. To compare the results, the measurements of the resin samples under the same conditions was also carried out. The measurements showed a similarity of amber and resin relating to their thermal behaviour. The large exothermal peak in resin and young amber samples showed that there are reactive compounds left in the samples. During million years these components diffuse out of the amber or react very slowly within the amber. During the exothermal reaction by-products may be formed which can crystallize and thus it could be measured in the second run. The different melting points of these by-products are related to the difference of chemical constitution of young amber and resin. The difference of enthalpy of reaction during the first run is caused by the same reason.

In the old amber samples there are no reactive components left. This shows the thermal behaviour of the two runs of the old amber samples. There is only a little exothermal effect being measured at a similar temperature and the glass transition temperature measured in the second run are approximately the same.

The comparison of the samples used in this paper show that at least their thermal behaviour changes infinitesimally after 60 million years. After that period of time the transformation of resin into amber is completed.

The diffusion of volatile compounds takes several million years and probably more than this and the organic compounds polymerize very slowly. This is shown by the calculation of the mean squared displacement of a diffusion process and by the exothermal effect in resin and young amber. To determine the correct age of amber it needs more measurements. This paper can show the connection of exothermal effects and the position of the glass transition temperatures to the age of amber and of resin, respectively, only in a qualitative way. To give a quantitative evidence about the age of amber more measurements must be taken by using different analytical methods at one kind of amber (e.g. Baltic Amber). For these measurements two methods present themselves in parallel to the DSC measurements. One is the IR analysis of amber to determine the concentration of reactive compounds left in the pieces in dependence of their depth to the surface. The other is the thermogravimetric analysis (TGA) to detect temperatures at which volatile compounds evaporate or a chemical reaction takes place. This method can be coupled with an analyzing instrument like an IR spectrometer to analyze the volatile compounds or the volatile byproducts of the exothermal reaction during the heating process. A comparison of these measurements might give a quantitative interrelation of the age of amber and its thermal behaviour.

Acknowledgements

We acknowledge the provision of all amber samples by Dipl. Chem. C. Lühr., Fachgebiet Instrumentelle Analytik of the Gerhard-Mercator-University Duisburg and Mrs Myintmyint Sein (m. Sc.) for correcting the English Text.

References

[1] R. Lewin, Die molekulare Uhr der Evolution. Gene und Stammbäume, Spektrum, Heidelberg, 1998.
[2] J.B. Lambert, J.S. Frye, G.O. Poinar Jr., Archaeometry 27 (1985) 43.
[3] S. Ritzkowski, Sonderheft Metalla, (1997) 19.
[4] G. Rehage, W. Borchard, Physics of glassy polymers, in: R.N. Harward (Ed.), Applied Science Publishers, London, 1973, p. 54.
[5] N.G. Savill, M.J. Richardson, British Polym. Journal 11 (1979) 123.
[6] E. Dobnik, Dissertation, Gerhard-Mercator-Universität-GH Duisburg, 1991, Duisburg.
[7] A.J. Kovacs, J.J. Aklonis, J.M. Hutchinson, A.R. Ramos, J. Polym. Sci., Polym. Phys. Ed. 17 (1979) 1097.
[8] R. Kosfeld, Angew. Chem. 83 (1971) 151.
[9] R. Kosfeld, L. Zumkley, Ber. Bunsenges. Phys. Chem. 83 (1979) 392.
[10] G. Rehage, Ber. Bunsenges 74 (1970) 796.