Journal of Thermal Analysis and Calorimetry, Vol. 59 (2000) 271–278

Dedicated to Prof. Edith A. Turi in recognition of her leadership in education

FREQUENCY DEPENDENCE OF THE DYNAMIC HEAT CAPACITY AT THE MELTING TEMPERATURE OF POLYETHYLENE CRYSTALS

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Abstract

The dynamic heat capacity of polyethylene was measured in the heating process over two decades of the modulating frequency using the light heating modulated temperature DSC. The dynamic heat capacity exhibited clear frequency dependence from 95°C to the end of the melting of the crystals. Frequency dependence of this work was compared with that of the quasi-isothermal measurement. The relaxation time estimated in this work was much shorter than that of the quasi-isothermal measurement. It was found that notable heat exchange between the sample and reference sides occurred between 120 and 135°C. Frequency dependence of the heat exchange was studied.

Keywords: frequency dependence, light heating modulated temperature DSC, polyethylene crystals

Introduction

Thermal analysis is an important technique for characterization of polymeric materials and its usefulness is described in detail in the book edited by Turi [1]. Differential scanning calorimetry (DSC) has been used as a standard and established technique and a wide variety of applications can be found in Turi's book. Recently modulated temperature DSC (MTDSC) was introduced [2, 3] and the field of application of DSC was extended. A significant advantage of MTDSC is an ability to separate the conventional DSC signal into the reversing and non-reversing components. This advantage has been utilized successfully in various studies. Another advantage, that has been pointed out from the early stage, is kinetic information that can be obtained from dependence on the modulation frequency. However, frequency range covered by the commercial instruments, typically from 0.01 to 0.1 Hz, is often not wide enough for the study of kinetics. We reported about another type of MTDSC called light heating modulated temperature DSC (LMDSC), in which light energy was used to generate the temperature modulation [4, 5]. LMDSC covered two decades of the modulation frequency. This paper is aimed to show a possible extension of application of DSC to the measurement of frequency dependence using LMDSC. Two subjects were studied. Firstly, heat exchange between the sample and reference sides was examined at

1418–2874/2000/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

various frequencies. Secondly, frequency dependence of the heat capacity was measured at a constant underlying heating rate and it was compared with the frequency dependence obtained by the quasi-isothermal measurement in our previous work [6].

It is known that the heat exchange occurs in the heat flux DSC because both the sample and reference materials are put on a metallic base plate. However, little attention has been paid to the frequency dependence of the heat exchange. In this study a technique to give periodic heat flow only to the reference side was used. This technique can be used in LMDSC because the light intensities for the sample and reference sides can be controlled independently from each other.

Frequency dependence during steady heating at a non-zero underlying heating rate was studied by Toda *et al*. using a commercial MTDSC instrument [7, 8]. It was found that the dynamic heat capacity was dependent on the underlying heating rate as well as the frequency. They covered effectively a wide frequency range by changing the underlying heating rate. However, their method is not successful if the relaxation strength and/or the width of the distribution of the relaxation time depend on the underlying heating rate. Therefore to establish a method of measurement that truly covers a wide frequency range will be useful for detailed studies of frequency dependence.

Experimental

Sample preparation

A pellet of a linear polyethylene (NIST 1475, M_w=52,000, M_w/M_n=2.9) was put between two polyimide films of 7.5 μm thick. The pellet was melted and pressed to form a thin plate of 0.17 mm thick including the polyimide films. After crystallization the surface of the polyimide films was not flat. This suggested that the surface of polyethylene was not flat after crystallization and the polyimide films were in good contact with polyethylene enough to trace the surface shape. The thin polyethylene sample with the polyimide films on both sides was cut and put in an aluminum pan with an aluminum lid on it. A very small amount of grease (high vacuum silicone grease from Dow Corning) was used to improve thermal contact between the polyimide films and the pan/lid. Thermal stability of the grease was confirmed to 200°C. Sample mass was 3.1 mg. On the reference side an aluminum pan to which a lid was fixed with a very small amount of grease was put. The pans were not crimped to avoid deformation of the bottom of the pan. Carbon was sprayed over the upper surface of the lids for light absorption.

Instrumentation

The LMDSC was developed in our laboratory using a commercial heat flux type DSC instrument (Rigaku, Thermo-Plus 8230) [5]. Heating and cooling was repeated between 80 and 170°C. Underlying heating and cooling rate was 1 and 3 K min^{-1}, respectively. The frequency was fixed during one heating and cooling scan. At the end of the cooling process the frequency was changed and the next scan was started without delay. The measured frequency was 0.01, 0.02, 0.05, 0.1, 0.2, 0.5 and 1 Hz. Integral time for Fourier transform was 200, 100, 40 and 20 s for 0.01, 0.02, 0.05 and 0.1 Hz and higher, respectively. Fourier transform calculation was made at every 20 s and the results were recorded in a computer. Measurement at 0.1 Hz was carried out two times, the first and last scans, to check reproducibility.

Two types of measurement were carried out. In the first type both the sample and reference sides were heated by the light, while in the second type only the reference side was heated. We derived the next equations in Ref. [6].

$$KC_{sr} = T_{sr}/T_s \tag{1}$$

$$T_s = T_{sr} - T_r \tag{2}$$

where all letters express complex quantities. T_{sr} and T_r are the amplitudes of the cyclic component of the temperature difference between the sample and reference sides in the first and second type measurements, respectively. C_{sr} and K are the heat capacity difference between the sample and reference sides and calibration parameter, respectively.

Results and discussion

Heat exchange

Figures 1 and 2 show the temperature dependence of the absolute value and the phase of $T_r(T)/T_r$ (140°C) where $T_r(T)$ is the measured value of T_r at temperature T. $T_r(T)$ are scaled to T_r (140°C) for comparing the results of different frequencies easily. The numbers of the vertical axis express the values of 0.01 Hz curve. Curves of other frequencies are shifted downwards to avoid overlapping each other. To calculate the right hand side of Eq. (1) $T_r(T)$ was approximated by a quadratic function of T to reduce the noise. This approximation was successful at frequencies equal to or higher than 0.2 Hz. However, at frequencies lower than 0.2 Hz deviation from simple curves

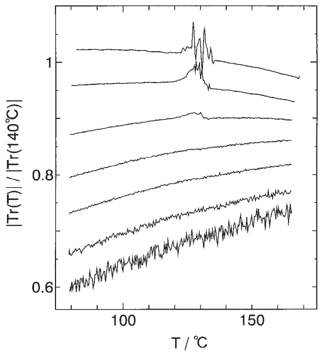

Fig. 1 Temperature dependence of $|T_r(T)|/|T_r(140°C)|$ at 0.01, 0.02, 0.05, 0.1, 0.2, 0.5 and 1 Hz (from top to bottom)

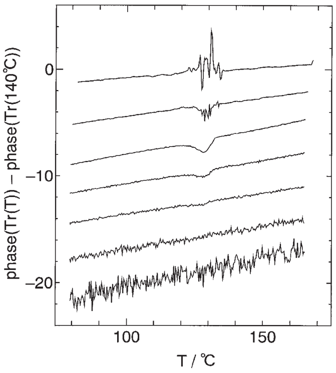

Fig. 2 Temperature dependence of the phase of $T_r(T)$ measured from the value at 140°C. The frequency of each curve was 0.01, 0.02, 0.05, 0.1, 0.2, 0.5 and 1 Hz (from top to bottom)

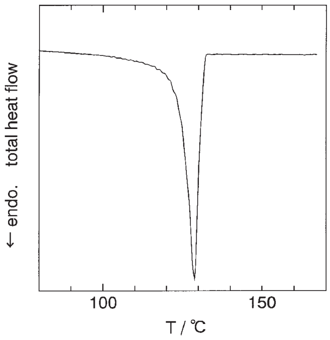

Fig. 3 Temperature dependence of the total heat flow

was observed between 120 and 135°C. As can be seen from Fig. 3 this temperature range corresponded to the melting on the sample side. Fitting of the quadratic function was made outside of this temperature range.

Deviation from the simple curve was composed of two components; one component changed slowly with temperature and the other component changed more quickly. The slowly changing component was attributed to heat exchange between the sample and reference sides. We considered as follows. The amount of the heat exchange increased with C_s that became larger in the melting temperature range because of the contribution from the latent heat. Since the amount of the heat exchange increased with T_r, the amplitude of T_r should have become large at the melting temperature. This was consistent with the results shown in Fig. 1.

It should be noted that, although the deviation from the simple curve was attributed to the melting, this does not mean absence of the heat exchange outside of the melting temperature range. If the heat capacity of the sample changes moderately with temperature, the effects of the heat exchange appear as a moderate function of the temperature. It can not be distinguished from the temperature dependence of the heat capacity of the sample and reference materials and the thermal properties of the base plate. This means that the heat exchange should be taken into account in theoretical studies of the instrument particularly at low modulation frequencies.

The origin of the quickly changing component was not clear. A possible origin we can suggest at present is poor separation of the observed signal into the conventional DSC signal and the cyclic signal. It is obvious that the separation becomes poorer as the averaging period becomes longer.

Dynamic heat capacity

Figures 4 and 5 show temperature dependence of the absolute value and the phase of the dynamic heat capacity, respectively. The dynamic heat capacity was scaled to the value at 140°C. The factor K in Eq. (1) was assumed to be independent of temperature. Results at the modulation frequency of 0.02, 0.1 and 1 Hz are shown. The 0.1 Hz curve shows the results from the first temperature scan. The last temperature scan at

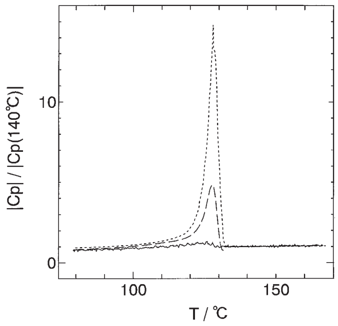

Fig. 4 Temperature dependence of the absolute value of the dynamic heat capacity scaled to the value at 140°C. Dotted, broken and solid lines show the curves of 0.02, 0.1 and 1 Hz, respectively

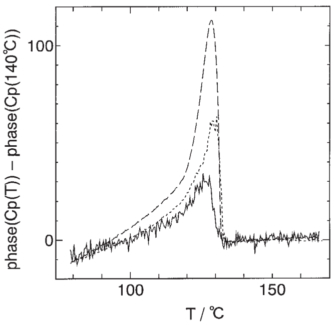

Fig. 5 Temperature dependence of the phase of the dynamic heat capacity measured from the value at 140°C. Dotted, broken and solid lines show the curves of 0.02, 0.1 and 1 Hz, respectively

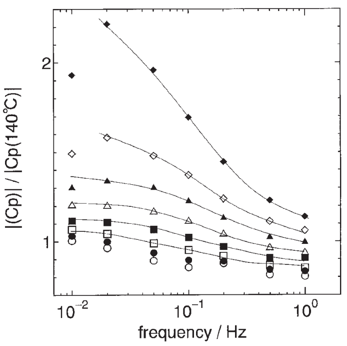

Fig. 6 Frequency dependence of the absolute value of the dynamic heat capacity scaled to the value at 140°C. o – 85°C, • – 90°C, □– 95°C, ■ – 100°C, Δ– 105°C, ▲– 110°C, ◇ – 115°C, ◆– 120°C

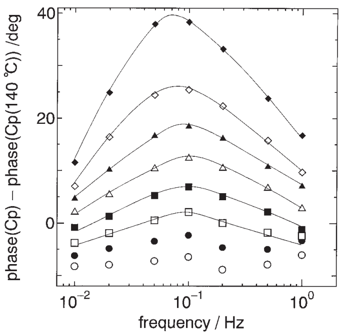

Fig. 7 Frequency dependence of the phase of the dynamic heat capacity measured from the value at 140°C. o – 85°C, • – 90°C, □– 95°C, ■ – 100°C, Δ– 105°C, ▲– 110°C, ◇ – 115°C, ◆– 120°C

the same frequency gave the results in good agreement with the first scan; the largest deviation in the absolute value and the phase was 2% and 1 degree, respectively. Significant frequency dependence was observed in the temperature range of the endothermic peak of the total heat flow (Fig. 3).

Figures 6 and 7 show frequency dependence of the absolute value and the phase at temperatures from 85 to 120°C at intervals of 5 K. At temperatures higher than 120°C approximation for $T_r(T)$ failed because of the heat exchange. In Figs 6 and 7 averaged values over successive ten data are plotted. The curves were not determined by calculation but drawn by rough fitting by eyes to show the tendency of the frequency dependence. Although the signal to noise ratio is not sufficiently good at 85 and 90°C, the curves of 95°C and higher clearly exhibit monotonous decrease in the absolute value and peaks in the phase. These are of a typical frequency dependence due to a relaxation process in the sample. It can be seen from Fig. 6 that the absolute value of 0.01 Hz was smaller than that of 0.02 Hz at 110°C and higher. This is not consistent with the frequency dependence of the relaxation process, but can be attributed to non-negligible heat exchange at the lowest frequency. It can be said that the highest estimation of starting temperature of the frequency dependence was 95°C.

The assumption of temperature independence of K is sometimes too simple. It is necessary to examine errors due to this assumption. Temperature dependence of K comes from two origins: temperature dependence of the thermal properties of the furnace materials and change in the thermal contact between the sample and the pan/lid accompanying the melting and the crystallization. If the first origin was important, frequency dependence should have been observed at temperatures higher than 140°C as well as at the lower temperatures. However, frequency dependence at 170°C was very small as seen in Figs 4 and 5. If the second origin was important, the effects of the thermal contact should have become larger as the frequency became higher. However, the frequency dependence of the phase had a maximum as seen in Fig. 7. These results showed that temperature dependence of K did not cause serious errors in the frequency dependence.

The dynamic heat capacity was measured quasi-isothermally at temperatures between 120 and 131°C at intervals of 1 K [6]. Frequency dependence was observed clearly. The relaxation time estimated from the frequency dependence was 14 s. On the other hand the peak position in Fig. 7 is about 0.1 Hz which corresponds to the relaxation time of 1.6 s. The peak position in Fig. 7 shifts slightly to the lower frequency direction as the temperature becomes higher. However, the amount of the shift is too small to explain the difference between the two relaxation times. In order to compare the measurement at a non-zero underlying heating rate and the quasi-isothermal measurement, an additional measurement was carried out; heating at the underlying heating rate of 1 K min^{-1} was stopped at 129°C and followed by the quasi-isothermal condition. The modulation frequency was 0.1 Hz. Result of this measurement is shown in Fig. 8. Starting time of the quasi-isothermal measurement

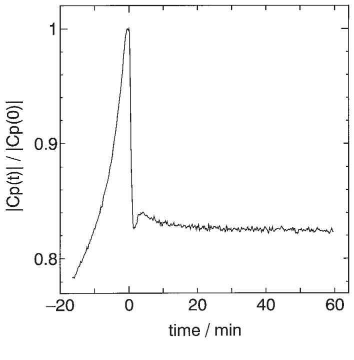

Fig. 8 Time dependence of the absolute value of the dynamic heat capacity at 0.1 Hz scaled to the value at the time of zero

was set to be zero. The absolute value of the dynamic heat capacity was scaled to the value at the time of zero. The absolute value decreased quickly at the beginning of the quasi-isothermal condition and reached almost constant value at 20 min. The relaxation time of the quasi-isothermal measurement was calculated from the data between 2000 and 3000 s after starting of the quasi-isothermal condition. Therefore it can be said that the state of the sample that gave the shorter relaxation time was notably different from the state that gave the longer relaxation time. It can be concluded at present that both the longer and shorter relaxation times are related to the melting process, but the two relaxation times correspond to different types of molecular processes; one is dominant during the steady heating and the other is dominant under the quasi-isothermal condition.

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